INVESTIGATION OF WATERFLOOD IMPROVEMENT FOR HEAVY OIL CARBONATE RESERVOIRS – CRUDE OIL/BRINE/ROCK INTERACTIONS

By

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ABSTRACT

Water injection has been used in the oil industry for a long time. This oil recovery method is considered relatively inexpensive and water is easy to inject, even in hostile environments such as high pressure/temperature or deep reservoirs. Compared to other oil recovery methods, water injection received less attention because it was assumed that there were neither reactions nor interactions with the reservoir fluids or reservoir rocks. This meant that the water, being immiscible with crude oil, was simply regarded as a way to displace the trapped oil. However, the use of water injection as a natural wettability modifier has recently gained significant attention, due to the discovery of the importance of physico-chemical interactions between the crude oil compounds and the water composition.

In this regard, the term smart water has been adopted for the idea of designing the injection brine composition in order to enhance oil recovery. Even though the alteration or modification of the composition of the injection water has been mentioned by various researchers, the findings and conclusions are not consistent. Whilst some laboratory and field applications have had successful outcomes, there are cases in which smart water was not found to make any significant difference.

The goal of this research was to investigate if some of the suggested mechanisms behind the smart fluids injection would apply to carbonate reservoirs, with a special focus on heavy oils. Occurrence of rock dissolution, as a mechanism for oil production, has previously been documented. However, the reasons for its presence have not entirely been found or described. This research shows that dissolution occurs as a direct and strong effect of the flow of injected water in contact with the crude oil. This work describes the results of a comprehensive set of experiments to investigate the importance and the extent of rock dissolution during water injection in carbonate heavy oil reservoirs. In addition, the results of the experimental work performed in this research with smart waters demonstrate that a substantial additional amount of heavy crude oil can be obtained under secondary as well as tertiary injection of appropriately designed water composition.

The findings from these experiments firstly revealed the generation of acidic water, which is derived from the interaction between injected fluids and crude oils. Further examinations showed that this acidic water is not detected by complex laboratory tests. Finally, it was also found that not all crude oils could generate the acidic water which is the cause of rock dissolution.

In this work, practical analysis helped to elucidate the real importance of the crude oil/injection water interactions. The laboratory tests that are presented essentially provide an insight into the impact of the chemical interaction between crude oil and injection water with the rock. The results suggest that the chemical interaction between crude oil and injected water may be one of the main reasons for the increased efficiency in response to the use of the smart waters for the improvement of oil production. The mechanisms that trigger the oil production for the studied crude oils in carbonate reservoirs may be linked to both changes of wettability and effect of the rock dissolution.

DEDICATION

To my dear Peque Saltamontes de las Verdes Praderas for her sacrifice and patience during these years. To my lovely family who were my first teachers, help to keep my feet on the ground and encouraged me to pursue my dreams.

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If I have seen further it is by standing upon the shoulders of giants. Sir Isaac Newton.

DECLARATION STATEMENT

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GLOSSARY

American Petroleum Institute	API
Back Pressure Regulator	(BPR)
Barrels	bbls
Carbon Dioxide	(CO_2)
Carbon Number Distribution	(CND)
Carbonic Acid	(H_2CO_3)
Centimetre	(cm)
Centipoises	cp
Characteristic Length	(L_c)
Core Diameter	(d)
Core Length	(L)
Could Heavy Oil Production with Sand	CHOPS
Cyclic Steam Stimulation	CSS
Differential Pressure	(ΔP)
Distilled Water	(DW)
Enhanced Oil Recovery	EOR
Environmental Scanning Electron Microscopic	(ESEM)
Expanding Solvent-SAGD	EX-SAGD
Feet	(ft)
Formation Water	(FW)
Hour	(hr)
Initial Permeability	(k_o)
Initial Water Saturation	(Swi)
Interfacial Tension	(IFT or σ)
International Energy Agency	IEA
Logarithmic Constant (Acid Dissociation Constant)	(pK_a)
Logarithmic Constant (Base Dissociation Constant)	(pK_b)
Low Salinity Seawater in Contact with Crude Oil “A”	(LSSW10CCOA)

Low Salinity Seawater in Contact with Crude Oil "E"	(LSSW10CCOE)
Low Salinity Seawater, 10 times	(LSSW10)
Low Salinity Seawater, 50 times	(LSSW50)
MiliDarcies	(md)
Milligram/litre	(mg/L)
Naphthenic Acids	(RCCOH)
Naturally Fractured Reservoirs	(NFRs)
Original Oil in Place	(OOIP)
Overburden Pressure	(OB)
Permeability	(k)
Porosity	(ϕ)
Pore Volume	(PV)
Psi	(lb/ft^3)
Saturates, Aromatics, Resins and Asphaltenes	(SARA)
Saturation Index	(SI)
Seawater	(SW)
Spontaneous Imbibition	(SI)
Steam-Assisted Gravity Drainage	SAGD
The United States of America	USA
Dimensionless Time	(t_D)
Toe-to-Heel-Air-Injection	THAI
Total Acid Number	(TAN)
Total Base Number	(TBN)
Viscosity	(μ)
Oil Viscosity	(μ_o)
Water Viscosity	(μ_w)
Water Alternating Gas Injection	(WAG)

LIST OF PUBLICATIONS

Sanchez-Rodriguez, J.; Gachuz-Muro, H.; Sohrabi, M. 2015. Application of Low Salinity Water Injection in Heavy Oil Carbonate Reservoirs. SPE- 174391-MS, the EUROPEC, Madrid, Spain.

Gachuz-Muro, H.; Sohrabi, M. 2014. Smart Water Injection for Heavy Oil Recovery from Naturally Fractured Reservoirs. SPE-171120-MS, Heavy and Extra Heavy Oil Conference, Medellin, Colombia.

Gachuz-Muro, H.; Sohrabi, M. 2013. Effects of Brine on Crude Oil Viscosity at Different Temperature and Brine Composition – Heavy Oil/Water Interaction. SPE-164910, the EAGE Annual Conference and Exhibition, London, UK.

CHAPTER 1 – INTRODUCTION

To this date, a vast amount of work has been published about the use of smart waters for carbonate oil reservoirs. By definition, smart water has been adopted as the idea of changing the injected brine composition in order to enhance oil recovery in the oil reservoirs. Smart waters have been considered as natural wettability modifiers, gaining significant attention from research groups and oil industry companies. Complex analysis such as micromodel tests, coreflood and spontaneous imbibition experiments and zeta potential, interfacial tension (IFT) or contact-angle measurements have been extensively run to explain the success of smart water for enhanced oil recovery methods. All of these have been used in research studies around the world in order to understand the mechanisms behind the improvement of oil production. Most of the studies on smart water injection have been conducted with light oils and have been focused on both sandstone and carbonate reservoirs. However, there are insufficient published reports in the literature on the application of smart water injections for heavy oils and extra-heavy oils in carbonate reservoirs.

The results of the range of investigations which have carried out, some of them contradictory, have allowed us to hypothesise certain mechanisms which are believed to be responsible of the good oil recovery factors. Computational programs, robust or unsophisticated, have also been used to simulate and represent such experimental results. Later, those same tools have been used to predict, find or validate previous mechanisms stated. However, sometimes, the answers to complex enquiries cannot be dealt with advanced tools or sophisticated experiments. First, we must learn to walk before we can run.

The aim of the work presented here is to experimentally investigate the performance of smart water injection for heavy oil recovery from carbonate rocks under high reservoir temperature. Five crude oils were assigned to this research, with different properties and similar reservoir conditions. Two specific crude oils were expressly selected for the complex experimental work. Limestone and Dolomite cores were also selected.

In this work, *Chapter 2* gives a general overview of the exploitation of heavy oils around the world. Next, a description of carbonate rocks that may contain hydrocarbons is presented. In addition, this Chapter also includes thermal and non-thermal methods used for enhanced heavy oil recovery in carbonate formations and naturally fractured reservoirs. Finally, the last part of this chapter presents short history of smart water injection and some proposed mechanisms affecting the efficiency of this process for different types of rocks.

The fluids, rocks and experimental methods which have been used for this research are all presented in *Chapter 3*. The properties of the cores and crude oils, brine compositions and descriptions of the tests and instruments used for this research will be presented in detail.

Chapter 4 describes the results of a comprehensive set of experiments to investigate the presence of rock dissolution during water injection in carbonate reservoirs. The findings from these experiments reveal the *generation of acidic water* which is derived from the *interaction between injected fluids and crude oils*. Some simplistic and practical tests show that this acidic water is not detected by complex laboratory tests. The effect of this generated water on rock dissolution is studied in 3 limestone cores.

Chapter 5 mainly presents a series of coreflood experiments that were performed using a group of carbonate cores, in which smart water injection was tested under both secondary and tertiary injection conditions. The experiments were conducted at 92^{o} C using two crude oils. A total number of fifteen tests are presented in this chapter (spontaneous imbibition and forced imbibition tests), in which the effect of smart water injection and the main mechanisms contributing to the oil recovery improvement are investigated. This chapter also focuses on contact-angle measurements, using both limestone and dolomite plates with two crude oils, together with a group of smart waters.

Finally, a summary of the conclusions is presented in *Chapter 6*, followed by a consideration of suggestions for future work.

CHAPTER 2 – LITERATURE REVIEW

INTRODUCTION

Until recent years, conventional crude oil reserves were accessible in large quantities. However, with lower oil prices, high oil demand and the low volume of oil discoveries in the last decade, the oil industry is targeting economical production of unconventional oil resources, amongst which heavy and extra-heavy oils are possibly the most important, due to existing oil volumes. Heavy and extra-heavy oils have long been dominated by the market price. Their exploitation has typically required alternative methods of production but the cost of these activities may be unattractive, and this has led to limited or delayed projects. Thus, heavy and extra-heavy oil deposits could represent a potential supply for both the short and long term.

Heavy and extra-heavy oil reservoirs are unconventional reserves of oil found in around 30 countries; Canada, Venezuela, the United States of America (USA), Mexico, Brazil, Saudi Arabia, Russia, Iraq and Kuwait are good examples. These oils are abundant and important. In 2005, the International Energy Agency (IEA) calculated that there were 6 trillion barrels of this type of oil in place. Most recently, the same Agency (2013) estimated that between almost 1,000 to 1,500 billion barrels (bbls) of unconventional oil resources remain to be recovered; this represents a vast energy resource.

When it comes to general properties, variations exist between heavy oil and conventional oils (medium or light oils). Heavy oil is dense and more resistant to flow but can flow in some fields with the assistance of lifting systems. It typically contains high levels of sulphur and certain metals, such as nickel and vanadium, which are the most commonly found.

The definition of heavy oil or extra-heavy oil varies according to who is defining it. In general, oil with $< 20^{o}$ API (American Petroleum Institute), is called heavy oil, while those with below 10^{o} API are regularly considered extra-heavy oils. The World Petroleum Congress (1983) describes heavy oil and extra-heavy oils based on their

viscosities and API densities at reservoir temperature. Hence, if it has an API grade less than 22.3^{o} API and a viscosity between 100 to 10,000 centipoises (cp), it is identified as heavy oil. Any oils with API density below 10 are called extra-heavy oils. The term bitumen (also called tar or oil sand) originated in Canada for extra heavy oils found in isolated areas. For simplicity, henceforward "heavy oil" will be used as a practical notation for heavy, extra-heavy oils and bitumen.

Heavy oils have been discovered in sandstones, carbonates and conglomerates. The most well-known reservoirs occur in unconsolidated sands with high permeabilities of the order of a few Darcies. These reserves of heavy oils are principally present in Canada, Venezuela, Russia and the United States. On the other hand, carbonate formations are much more complicated and may be massively fractured and include vugular zones. Mexico and Brazil possess large concentrations of such heavy oil reserves. More than 80 percent of Mexico and Brazil's oil production occurs offshore and consists of heavy oils. The Wafra and Ferdows fields in the Middle East are also examples of carbonate rocks with reasonably heavy oil deposits (Buza, 2008).

Most of the oil companies are trying to produce as much as possible under natural conditions (primary production), but these types of reservoirs require specialised production methods. Natural heavy oil recovery generally yields low recovery factors. Lu et al. (2010) observed that primary production from heavy oils is concentrated in the range of 5 to 10 % for a group of clastic reservoirs, as shown in Figure 2.1. Alternative production methods have included mining technology, horizontal and multilateral wells, cold production with artificial lift systems, and cold heavy oil production with sand (CHOPS) or others. It is patent that the fundamental complication in recovery is the high viscosity. The more viscous the oil is, the more difficult it is to recover. Any decrease in viscosity will improve the oil mobility, leading to a rise in the oil recovery factor. In this case, the temperature has a significant impact on the oil viscosity. If the temperature increases, the oil viscosity drops and this may improve the flow of oil from the reservoir to the wells and finally to the surface.

Once extraction by natural production methods has finished, it is necessary to execute alternative methods of oil recovery. Secondary recovery by water injection in heavy oil reservoirs is another option. Typical recovery factors for water injection range from 5 to

54 % (Lu et al., 2010; Alvarez et al., 2013). The figure does not exceed 40 % of oil recovery and normally fluctuates between 20 to 40 %. The major obstacle is the higher mobility of water, creating the viscous fingering effect. This would lead to poor sweep efficiency, resulting in low oil recoveries.

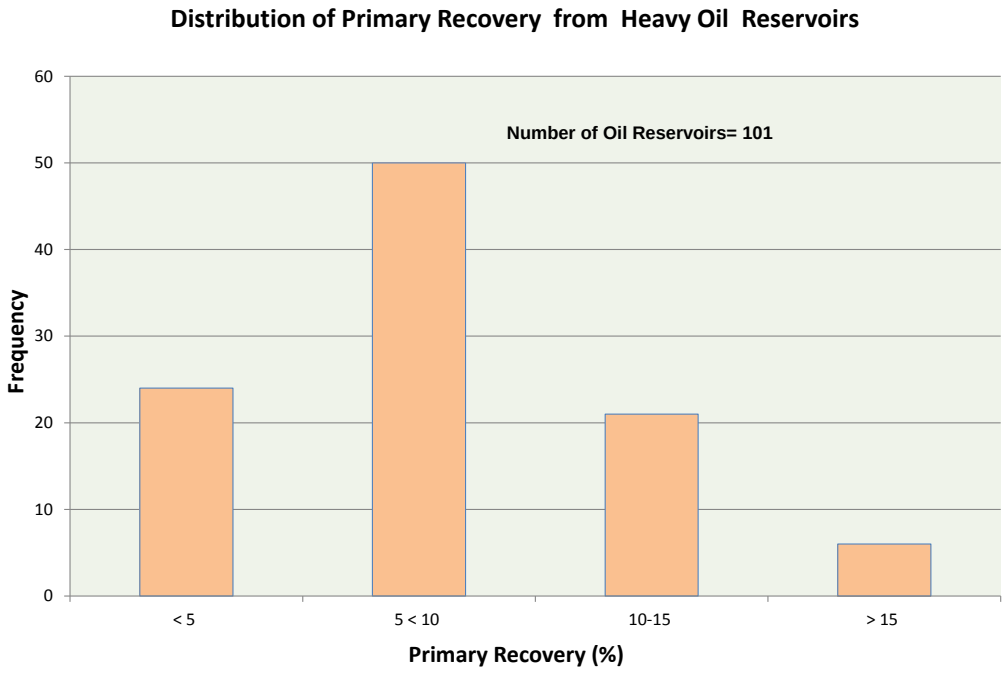

Figure 2.1: Distribution of primary recovery from heavy oils reservoirs (Modified from SPE-130758, 2010).

As pointed out above, the most promising solution to improve the oil recovery would be to reduce the viscosity, thus generating better exploitation conditions. For this reason, thermal methods have been extensively applied for heavy oils. These methods include cyclic steam stimulation (CSS), steamflood, steam-assisted gravity drainage (SAGD), hot water and in situ combustion. Additionally, some new techniques are ongoing but are not yet commercial, such as the use of solvents, electrical resistance, the combination of vertical and horizontal wells or a fusion of methods, such as Expanding Solvent-SAGD (EX-SAGD) or Toe-to-Heel-Air-Injection (THAI). However, their counterparts are the non-thermal methods, which have both benefits and restrictions. For instance, steam injection covers a greater area than CSS, retrieving up to 50 % of Original Oil in Place (OOIP), according to Nasr et al. (2005). This last method (CCS) is lower in efficiency than the others, with between 15 to 20 % recovery. SAGD, which has been applied in Canada, is one of the fastest growing methods. Recovery factors of

above 50 % may be expected (Cunha, 2005). In situ combustion has been tested with great success in Rumania (Panait-Patica et al., 2006) and has produced reasonable results in other oil fields around the world (Chu Chieh, 1982). Apart from technical limitations such as steam or air generation, reservoir depths, well spacing, and working in offshore fields, other factors are also expected to arise as oil production develops. For instance, these factors could be the use of water, increase CO_2 emissions, and safety and environmental issues.

In the last 12 years, the production of heavy oil has been economically attractive for companies. The available thermal processes and oil production were more advantageous with a high cost-benefit. However, the current oil market has motivated oil companies to postpone or cancel their projects, due to the dramatic collapse of prices at the beginning of the year of writing. As heavy oil normally sells at a lower price than medium or light oils, companies are battling to cover the cost of production, operation and transportation. Even so, some of them are continuing to produce heavy oil with losses at current prices. This has provoked oil operators to look into moving into large-scale and safe projects where the use of inexpensive methods or technologies may mitigate the impact of the low prices. Hence, it is essential that each production process is adapted to the need of the local conditions under economically suitable schemes.

Recently, extra interest has emerged in efficiently using other non-thermal methods for Enhanced Oil Recovery (EOR) Processes. Overall, employment of water and CO_2 may offer convenient, functional and economical options for extracting heavy oils. For decades, water has been injected into oil reservoirs as an efficient and cost-effective way to prolong the productive life of an oil reservoir. Although, from a practical point of view waterflooding is relatively straightforward, interactions between injected water and the reservoir rock and fluids can be quite complicated and sometimes unexpected behaviours are observed. This indicates that, despite extensive research and field applications of water injection, to date, our understanding of the process remains incomplete. Recent investigations have shown that the composition of the water can have a significant impact on the oil recovery achieved by water injection (Jadhunandan et al., 1995; Yildiz et al., 1996, Austad et al., 2005; Tweheyo et al., 2006; Fathi et al.; 2011). Most of the available research results are on light oil systems, whereas the impact of water composition and its interactions with heavy oil has barely been

investigated (Abass et al, 2013; Gachuz-Muro et al, 2014; Sanchez-Rodriguez et al., 2015). Nonetheless, there is no doubt that the injection of water has helped oil recovery in many favourable ways throughout the oil industry.

Apart from water injection, CO_2 injection systems have also been demonstrated to be beneficial in commercial applications, for more than 30 years. As of 2014, there were 177 CO_2 projects in the U.S.A. with a total additional oil production of 335,530 barrels per day (Koottungal, 2014). This shows the increase of their application over the past 8 years. Independently of the type of scheme used for CO_2 injection, such as pure CO_2 injection, carbonated water, water alternating gas injection (WAG) or Huff and Puff, it is an efficient EOR technology, achieving up to 83 percent of heavy oil recovery (Farzaneh et al., 2015). To be a viable project, its operation is linked to the availability and cost of CO_2. Many other non-thermal processes have been suggested but they have not been as successful as CO_2 or water injection, for a variety of reasons.

Under the existing conditions, the non-thermal methods seem to be appropiate options for the development of heavy oil fields. Water injection looks promising and could in effect be an aid to convert these special oil fields into potential oil fields. Water offers enormous advantages: the key benefits of this system would be the low cost and the availability of the water reserves, in particular for carbonate formations, where such exploitation schemes may have more importance.

This chapter will briefly cover a description of carbonate rocks. The next section will also include thermal and non-thermal methods used for enhanced heavy oil recovery processes in carbonate formations. The last part of this chapter will contain a short history of smart water injection and some proposed mechanisms affecting the efficiency of this process for different types of rocks.

2.1 CARBONATE ROCKS

Carbonate sediments have a wide variety of particle size, because they were formed by organic activity and redistributed by transport. Porosity values may range from 40 % to 75 % and permeabilities from 200 to 30,000 md (Lucia, 2007). Their multiple pore size

distribution means they have a wide range of permeability values for the same porosities. Three forms of carbonate are mainly present in aragonite, calcite and magnesium. Carbonate rocks generally consist of 3 types of rocks: a) limestones, which are composed of calcite (at least 50 % of calcium carbonate) and other materials in minor concentrations; 2) dolostones, composed of a high amount of dolomite mineral (50 % >) and small particles of other minerals and 3) chalks, which are composed of more than 90 % of calcium carbonate. Their origins are varied and they are also soluble when water is slightly acidic. Waters that are low in pH (acidic water) can have undesirable effects on these formations. These waters may promote the dissolution of calcium carbonate.

Dolostone formations (Figure 2.2) especially, undergo changes after their deposition. Originally, the sedimentary rock is deposited as calcite or aragonite, then, due to diagenesis is modified to dolomite (a process called dolomitisation). This modification allows it to create a secondary porosity. Thus, the flow of fluids is the determinant in the origin of dolomite constitution. Chalk is a soft and pure limestone, fine grained, with excellent porosity and low permeability. These rocks are formed from coccolith biomicrites.

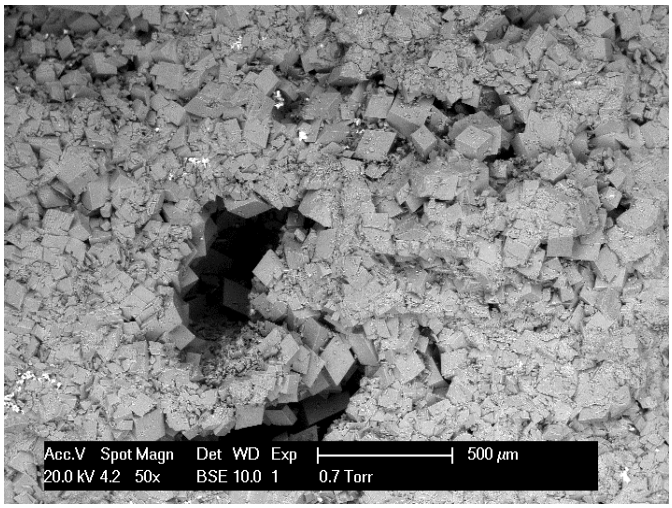

Figure 2.2: SEM image of a dolomite fragment.

In general, carbonate rocks offer exceptional petrophysical properties which make them good candidates for accumulating hydrocarbons and most of them are frequently associated with fracture systems. The presence of two systems, one known as a matrix

and another called the fracture system, create special production characteristics, which fundamentally differ from those of conventional reservoirs. Therefore, hydrocarbon production in naturally fractured reservoirs (NFRs) is governed by the interactions between the matrix and the fractures.

The Cantarell (Rodriguez and al., 2001) and Ku-Maloob-Zaap Complex in Mexico (Perez-Martinez, et al., 2012), Haft Kel field (Saidi, 1987-1996) in Iran and the Ekofisk Complex in the North Sea (D'Heur, 1984 and Sulak, 1991) illustrate typical examples of naturally fractured carbonate reservoirs.

2.2 EOR IN CARBONATE RESERVOIRS

Enhanced Oil Recovery (EOR) methods vary significantly from one type of reservoir to another. Last year (2014), according to the Oil & Gas Journal, there were 199 active EOR projects in the United States of America, most of them focused on the gas injection. Due to CO_2 accessibility of natural resources, the additional volumes of CO_2 from the industry, the construction of pipelines and, of course, a positive outlook for the oil market, the use of CO_2 injection was expected to be expanded; however, the collapse of the oil prices has negatively impacted the development of new projects around the world.

According to Manrique et al. (2010), the use of EOR processes has been mainly applied to sandstone reservoirs, where thermal methods predominate in their application, Figure 2.3. Conversely, gas injection has been more popular for carbonate formations. Water injection in some carbonate reservoirs has led to good recovery levels, including in NFRs.

Sun et al. (2003) reviewed the ultimate recovery efficiency in 213 mature carbonate fields. Thirty-six percent of oil, on average, is recovered from carbonate oil reservoirs, as shown in Figure 2.4. However, they also reported that the recovery factor for heavy oil carbonate reservoirs is less than 30 %.

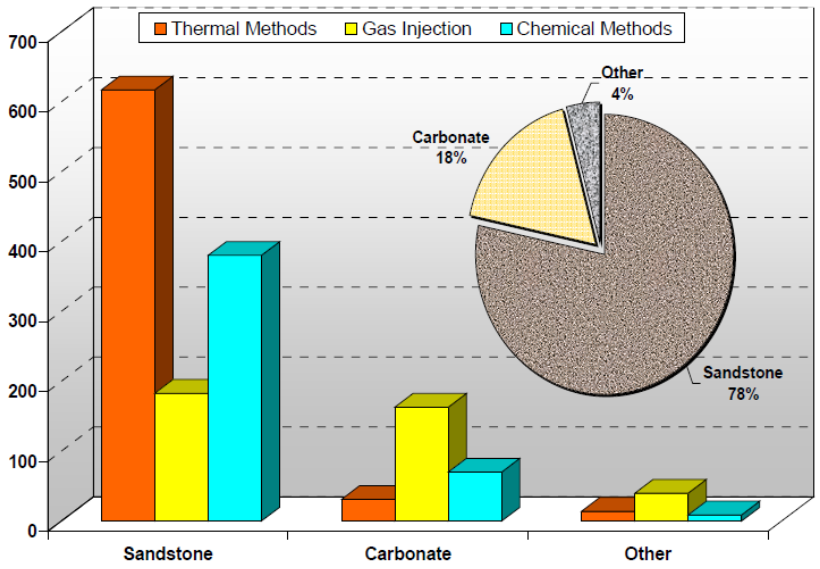

Figure 2.3: EOR field projects (Adapted from SPE-130113, 2010).

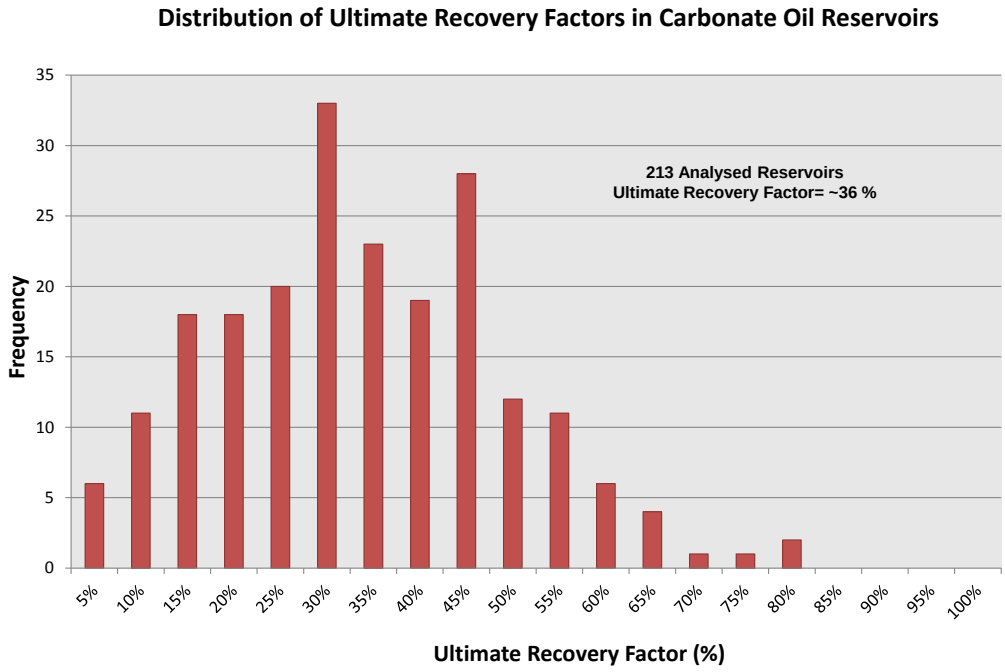

Figure 2.4: Distribution of ultimate recovery factors in carbonate oil reservoirs (Modified from SPE-84459, 2003).

2.2.1 EOR in Naturally Fractured Carbonate Reservoirs

Carbonate oil reservoirs comprise a heterogeneous, essentially fractured, low permeability matrix, with the presence of vugs and sometimes partially dolomitised. These characteristics, along with oil-wet conditions and high rates of oil production result in low recovery factors. In naturally fractured carbonate reservoirs, the oil is produced from and by the fracture systems in the reservoir and the oil in the matrix remains practically unaffected. In general, reservoir management is possibly the key factor in maximizing the recovery factor in NFRs. The major mechanisms involved in the oil recovery process were explained by Lemonnier and Bourbiaux (2010). Oil from fractured reservoirs may be produced under a combination of various processes, either natural mechanisms such as water drive and gas expansion or enhanced oil recovery methods. As stated by these authors and previously by Firoozabadi (2000), the main difference between fractured and non-fractured reservoirs is the capillarity phenomenon, which dominates the matrix-fracture interaction.

Allan et al. (2003) evaluated one hundred fractured reservoirs from around the world to establish how the recovery factor is influenced by reservoir and fluid properties. The NFRs were organized into four groups, based on their permeability and porosity ratio. Figure 2.5 shows the final recovery factors for 56 fractured oil reservoirs. The common aspect is the low oil production, expressed as between 0 to 30 %.

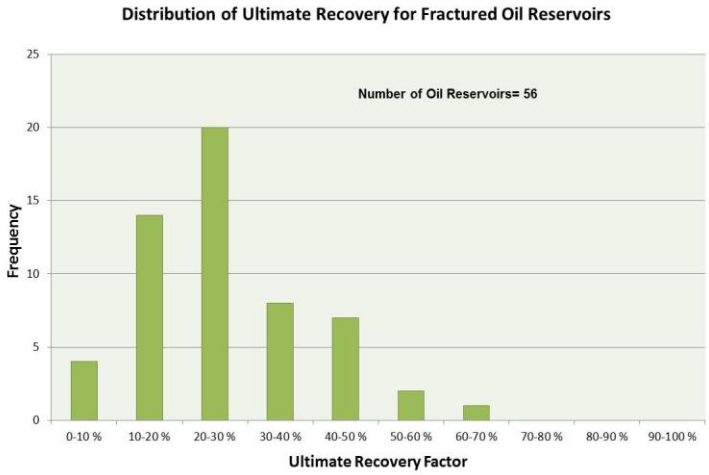

Figure 2.5: Distribution of ultimate recovery factor for fractured oil reservoirs of all types (Modified from SPE-84590, 2003).

Other classifications for NFRs have also been made by van Golf-Racht (1982), Nelson (2001), Aguilera (1999) and recently Bourbiaux (2010). Aguilera, particularly described typical oil recoveries based on the percentage of original oil in place. He included depletion drive as one of the main mechanisms for the oil recovery. For instance, depletion drive plus other natural mechanisms such as gravity segregation or water drive may have the highest recovery factors (between 30 to 60 % or more), whilst oil reservoirs with depletion drive or natural depletion plus injection of gas may have lower final recovery factors, ranging from 10 to 30 %.

The gas injection EOR processes, particularly, have shown good opportunities to revitalize carbonate oil fields and NFRs around the world (Manrique et al., 2006 and 2010). For instance, CO_2 injection has been remarkably successful for improving light oil recovery and also for heavy oils (Karaoguz et al., 1989). However, the cost of gas supply and injection can be prohibitive. Water injection, especially seawater, has been efficient in carbonate reservoirs in the North Sea (light oils). The success of water injection has been attributed to the water being imbibed into the matrix, changing the wettability of the system (Austad, 2007). This implies that the imbibition process and wettability alteration may be the most reliable mechanisms to reach the extra oil that is retained in the rock matrix.

It is clear that the objective in NFRs is to produce hydrocarbons from the matrix, because it is considered that, at present, ~ 90 % of the oil recovered is from the fracture network with lower oil production from the rock matrix (Garcia et al., 2006). Nevertheless, other unfavourable conditions may affect the efficiency of the recovery processes. These could include the presence of heavy oils, high pressure and temperature conditions or strongly oil-wet systems.

2.2.2 EOR in Heavy Oil Fractured Reservoirs

Heavy oil reservoirs are amongst the oil reservoirs that usually undergo EOR early in their production life, due to their viscosity. That is because these reservoirs rarely produce under natural (primary) recovery mechanisms and sometimes even react inadequately to secondary recovery methods. What is more, NFRs containing heavy oils

would be amongst the most difficult reservoirs to produce from, and this often leads to very poor reservoir performance with low recovery factors. For instance, thermal recovery methods (e.g., steam injection) are usually applied to this type of reservoirs, especially in sandstone formations, where they are mainly found. Based upon a study of 120 clastic reservoirs, Lu et al. (2010) concluded that the thermal methods were mainly used for heavy oils (with recovery factors between 9 and 79 %). These thermal methods cannot be successfully or economically applied to every heavy oil reservoir, because of certain limitations. There is, therefore, a great interest in developing non-thermal methods for improving heavy oil recovery. Lu and his colleagues also reported that water injection yielded between 20 to 45 % more oil. This last method was economic and its practice has been extended to deeper reservoirs (Figure 2.6).

Non-thermal methods such as nitrogen (Rodriguez et al., 2001) and CO_2 (Karaoguz et al., 1989) injection have been applied to heavy oil reservoirs with great success, but the volumes of these gases required and the costs control their use.

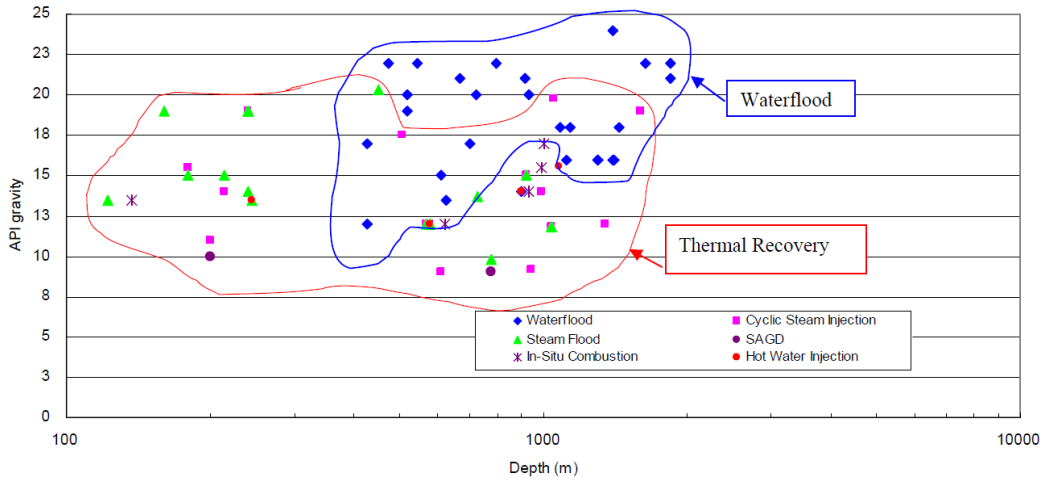

Figure 2.6: API gravity vs depth for heavy oils (Adapted from SPE-130758, 2010).

Water injection is considered relatively inexpensive and water is easy to inject, even in hostile environments such as high pressure/temperature or deep reservoirs. It can also be implemented at any time during the reservoir life. As seen above, waterflood has been a regular method for heavy oils in clastic reservoirs with modest recovery factors. For NFRs, however, the application of water is under constant debate, because so many taboos developed around its injection. The main issue is its early water breakthrough in the oil production wells with high water cuts, after some years of operation, but it has

largely been effective in water-wet reservoirs. In 1987, Saidi asserted that water imbibition in naturally fractured reservoirs was ineffective. This assumption was founded on particular studies. However, to date, the North Sea fields are good examples of successful water injection programmes in naturally fractured carbonate reservoirs, where some of these exhibit intermediate or oil wet conditions. Evidently, the seawater injection in the fractured Ekofisk field (Sulak, 1991) was a fruitful injection process.

Thus, there is a great need to improve the oil recovery from heavy oil fields, and the use of non-thermal methods could provide valuable additional recovery factors for these unconventional reservoirs.

2.3 SMART WATER: HISTORY AND MECHANISMS OF ENHANCED OIL RECOVERY

2.3.1 History

Water has been used in the oil industry for a long time. As pointed out, this method is considered relatively inexpensive and water is easy to inject, even in hostile environments such as high pressure/temperature or deep reservoirs. Since the late 19th century, water injection has been used to maintain reservoir pressure and it was recognised that it had the ability to improve oil recovery, but it was not until the 1930s that some injection methods were commenced. Initially, the practice was to reinject the produced water into the reservoir; later, water was brought in significant quantities from nearby oil reservoirs, rivers or oceans. The water injection was well appreciated but received less attention because it was assumed that there were neither reactions nor interactions with the reservoir fluids or reservoir rocks. Water, immiscible with crude oil, was simply regarded as a way to displace the trapped oil. So far, water injection has been responsible for a considerable amount of the oil produced around the world. In fact, during the 20th century, most operators began to investigate the feasibility of the water injection, following the natural depletion of the fields.

The use of (smart) water injection as a natural wettability modifier has recently gained significant attention. The term smart water has been adopted as the idea of changing the

injected brine composition in order to enhance oil recovery in the reservoirs. Smart water may be classified into: a) water with lower salinity or ion composition (< 5000 ppm) or b) a certain type of water with high salinity, which undergoes a modification of its original composition. To date, seawater has been incorporated as a part of this group of smart waters, due to its important role of being a natural wettability modifier. Low salinity water or diluted water has also been employed, with different names, such as LoSal, by British Petroleum (Robertson, 2007), Designer WaterFlood, by Shell (Ligthelm et al., 2009), Advanced Ion Management, by ExxonMobil (Gupta et al., 2011) or Smart Water Flood, by Saudi Aramco (Yousef et al., 2012); in each case, the concept is basically the same.

Studies on smart fluids go back to the 1940s, when Smith (1942) analysed the effect of different brines injected into sandstones with a wide range of permeabilities. The oil recovery was less effective for the fresh water. In 1957, Martin observed better recoveries by injecting fresh water, ascribing such improvements to swelling and migration. Later, Bernard (1967) performed some experiments with fresh water and sodium chloride. The oil recovery was linked to a rise of differential pressure and/or swelling clay effects. During the 1990s, Morrow and his group extended these previous studies and examined how a lower brine composition can affect oil recovery (Morrow, 1990, Jadhunandan and Morrow, 1995; Yildiz and Morrow, 1996; Tang and Morrow, 1997 and 1999; and Yildiz et al., 1999). Morrow and colleagues confirmed with more than 50 coreflood experiments that brine salinity and composition were impacting the rock wettability. They also noticed a change of wettability when low salinity water was used (Tang and Morrow, 1997). Two years later, they identified some conditions for the influence of low salinity, centered on the presence of connate water, a mixed-wet system and presence of clay content. Since then, many technical papers on smart water have been published. Low salinity water injection is widely being studied by various research groups and the level of investigation is being expanded substantially. The mechanisms are still the subject of debate; however, the hypothetical causes proposed in the literature can be categorized as chemical reactions between rock-formation brine-injected water-crude oil that may lead to wettability changes.

Even though the alteration or modification of the composition of the injection water has been mentioned by various research groups, the findings and conclusions are not

consistent. For instance, in carbonate reservoirs, seawater worked at high temperatures and about 33,000 ppm total salt content, but affected the initial wettability in sandstones when diluted to much a lower salinity < 5000 ppm. Clearly, other factors such as crude oil composition, rock mineralogy and formation and injected water chemistries affect the wetting properties of oil reservoirs. Whilst some laboratory and field applications have had successful outcomes, there are cases in which smart water was not found to make any significant difference.

2.3.2 Proposed Mechanisms for Smart Waters

There are numerous technical papers on this topic, in which researchers have proposed many mechanisms, but at this time, the real mechanisms or combination of mechanisms which lead to improving the oil production have not been plainly defined or identified. Various researchers have come near to explaining the reasons, but controversies dominate the published literature. Although, there is general consensus that the complexity of the fluids/rock system is governing the effects, much fundamental knowledge is lacking and many questions and uncertainties remain. It is not clear from the various references which mechanism or mechanisms work in specific rocks, fluids or conditions.

In recent years, particularly in the last 10 years, systematic studies by Austad and his research group, (2005, 2006 and 2011) have verified that seawater is able to alter the wettability of some carbonate rocks. The presence of SO_4^{2-}, $Mg^{2+}$and Ca^{2+} ions in seawater helped to improve oil recovery at temperatures above 90^{o} C. Most of their reported studies were focused on fluid/rock interactions. The experimental results gave solid reasons to defend their theory. The seawater injection research work has primarily been carried out in Norway. Research has also shown that ionic composition can play a vital role in oil recovery and may yield up to 85 % of total oil under tertiary recovery mode (Austad et al., 2005-2007; Puntervold et al., 2009; Rezaei Doust et al., 2009; Shariatpahahi et al., 2010-2011; Tweheyo et al., 2006; Zhang et al., 2007).

The studies of smart water as diluted water injection have been focused on sandstone reservoirs and more recently have been expanded to carbonate rocks (Austad et al., 2010 and 2012; Fathi et al., 2011; Romanuka et al., 2012; Strand el al., 2008; Yousef et

al., 2010-2012; Zhang et al., 2012). Several mechanisms have been inferred as responsible for the diluted water injection effects. Tang and Morrow in 1999 observed an improvement in oil production. They explained the first mechanism for diluted water injection based on fines migration. Since then, other research groups have envisaged different mechanisms; some of these are shown in Figure 2.7. A comprehensive description of other mechanisms is summarised by Austad and al. (2010) and Sheng (2014).

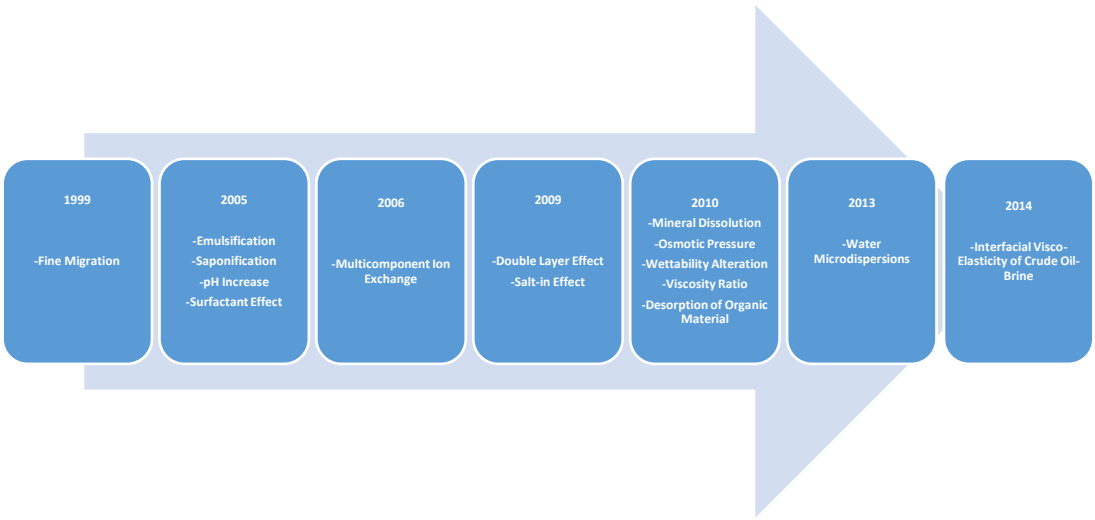

Figure 2.7: Overview of low salinity water mechanisms.

Even though there is evidence of an increase in oil recovery, some smart water experiments have not observed certain mechanisms such as fines migration, mineral dissolution or effects such as differential pressure changes or increased pH. Other mechanisms have been ruled out (Lager et al., 2006; Zhang et al., 2007; Boussour et al., 2009; Cissokho et al., 2009; Austad et al., 2010). Yousef and his colleagues (2010-2012) have examined water injection to enhance oil recovery in carbonate rocks. They modified the composition of the seawater and found that both secondary and tertiary modes look promising. They also affirmed that wettability alteration was the main mechanism. Coreflood experiments and interfacial tension (IFT), contact angle and zeta potential measurements were all evaluated and used for their analyses. Similar results have been reported by other groups, all indicating good recovery factors in carbonate cores (Romanuka et al., 2012; Zahid et al., 2012; Al-Attar et al., 2013; Shehata et al., 2014). It seems to be that wettability change is the final result of other mechanisms (Morrow and Buckley, 2011) and is the most commonly responsible mechanism indicated by researchers.

So far, the smart water experiments have revealed its significant advantages and have indicated that the injection process can give unknown local changes which may affect the oil recovery. Thus, it is difficult to generalise that smart water injection can be applied to all systems under all conditions. Moreover, most of the laboratory tests on smart water injection have been conducted with light oils, but there are no published reports in the available literature on the application of smart water injection for heavy or extra heavy oils. Some efforts has been made, for example, in Sudan (Abass et al., 2013) where it was indicated that more than 25 % of additional oil could be recovered by injecting low salinity water as an alternative recovery method, or the United Kingdom (Gachuz-Muro et al., 2014; Sanchez-Rodriguez et al., 2015), where experimental work and simulation analyses have been conducted leading us to believe that similar mechanisms may operate in heavy oil carbonate reservoirs.

Therefore, the goal of this dissertation is to investigate if some of the suggested mechanisms behind the smart fluids could be present for carbonate formations, with a special focus on heavy oils. In addition, the experimental research presented in this PhD dissertation is intended to improve the knowledge and understanding regarding some of the mechanisms believed to be the causes of the increased oil recovery provided by smart waters, giving the reasons why and how such mechanisms are generated.

CHAPTER 3 – EXPERIMENTAL WORK

In this chapter the materials employed such as crude oils, brines, rock and solvents and the experimental methods will be described briefly.

3.1 MATERIALS

3.1.1 Cores

Most of the work in this thesis has been performed on limestone and dolomite rocks. Table 3.1 summarises a list of the dimensions and properties of the limestone and dolomite cores used for the experimental tests. Their dimensions were measured and porosity and brine permeability were determined by measuring the differential pressure across each core at different flow rates in a special core holder designed for high pressure and high temperature.

Table 3.1: Properties of cores used for laboratory experiments.

Core Number	**Diameter (cm)**	**Length (cm)**	**PV (ml)**	**ϕ (%)**	**k_{brine} (md)**
Limestone					
Lim-1	2.51	15.20	14.29	19.00	41.13
Lim-2	2.51	15.15	15.21	20.26	19.47
Lim-3	2.51	15.20	14.10	19.00	34.65
Lim-4	2.55	15.30	16.58	21.21	6.90
Lim-5	2.50	9.70	17.91	37.42	19.51
Lim-6	2.64	15.20	20.11	24.17	51.80
Lim-7	2.51	15.20	16.36	21.75	20.89
Lim-8	2.52	15.20	15.55	20.64	19.40
Lim-9	2.52	15.20	18.34	24.25	146.51
Dolomite					
Dolom-1	2.62	15.20	17.04	20.79	194.32
Dolom-2	2.60	15.30	21.42	26.37	345.49
Dolom-3	2.61	15.30	15.57	19.03	28.49
Dolom-4	5.09	15.20	58.15	18.80	142.21

Mercury injection was used to obtain pore structure data for each core type. The cores showed great differences in both properties and pore structure. In general, the limestone cores were consistently homogeneous. Pore throat frequency analysis showed a wider pore size distribution compared to the dolomite cores. This limestone rock has pore sizes in the range from 0.01 μ to 100 μ, with peaks at 0.3 μ and 17 μ. On the other hand, the dolomite cores were more heterogeneous. Pore structure analysis exposed two specific regions, a limited distribution of less than 2 μ and a more widely distributed section of pore size between 2 to 100 μ, giving the variety of permeability values for this type of used cores.

The Environmental Scanning Electron Microscope (ESEM) revealed that the limestone cores contained carbon, oxygen and calcium, and also small magnesium and silicon concentrations were noted, whereas the dolomite rocks consisted of carbon, oxygen, magnesium and calcium with small amounts of iron and silicon. Figures 3.1 and 3.2 show the mineralogy of the rocks. Although the presence of sulphate was not detected using this method, chemical analysis of the effluents during the water saturation confirmed the presence of this anion in originating from the cores.

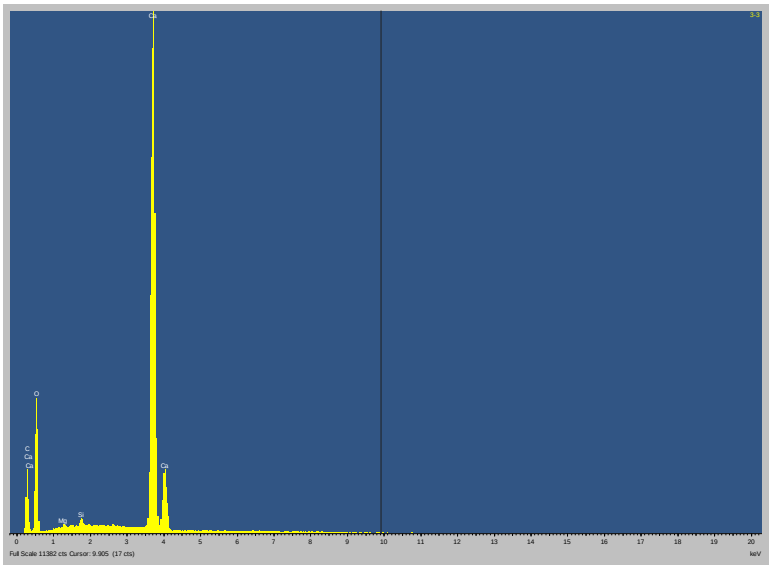

Figure 3.1: Mineral composition of limestone cores.

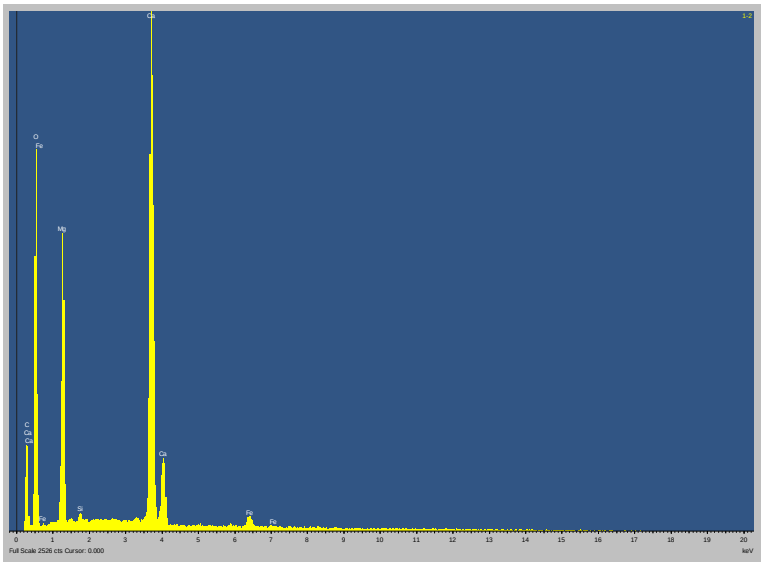

Figure 3.2: Typical mineral composition of dolomite cores.

Additionally, to determine contact angle measurements, both dolomite and limestone plates were obtained from tight core samples. The plates (25 x 25 x 4 mm, approximately) were polished and cleaned.

3.1.2 Crude Oils

Different heavy oil samples were selected from a group of reservoirs and tested in this work. Table 3.2 shows the basic properties of the crude oils. The total acid and base numbers are also presented. The crude oils were centrifuged before being used, to ensure they were free from solid particles or emulsions. Wax or other deposits were not observed in the crude oil samples.

Table 3.2: Crude oil properties.

Crude Oil	Density* (^{o}API)	Viscosity* (cp)	Asphaltene Content (% wt)	Water Content (ppm)*	Resins Content (% wt)	TAN (mgKOH /g)*	TBN (mgKOH /g)*
A	14.12	53,484.31	13.20	208.40	31.70	1.00	3.50
B	12.49	71,253.86	27.78	302.46	28.29	0.17	4.23
C	15.44	295,328.67	24.00	2,619.30	17.6	0.35	4.60
D	32.18	15.60		199.00		0.21	0.21
E	19.27	1,251.80	0.82	2,920.52	16.85	2.40	2.10

*Measured at 20^{o} C.

The composition of the original crude oils was also determined in terms of asphaltenes, resins, aromatics and saturates. Although some analyses of metals and sulphur content of certain crude oils were obtained, they will be presented later.

3.1.3 Brines

Brines were reformulated from the original compositions in the laboratory, using distilled water and salts. Four brine solutions with different compositions were prepared for this work. In order to have a reference system for some experiments, distilled water (DW) was also used. The seawater used for the experiments was from the Gulf of Mexico. Table 3.3 depicts the composition of each brine. Seawater (SW) brine contains significant amounts of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions but the formation brine (FW) brine only contains small amounts of Mg^{2+} and SO_4^{2-}.

Table 3.3: Brine compositions.

Ion	**FW (mg/L)**	**SW (mg/L)**	**LSSW10 (mg/L)**	**LSSW50 (mg/L)**	**Distilled Water (mg/L)**
Na^+	9,614.97	11,429.38	1,142.93	228.58	-
Ca^{2+}	320.36	429.60	42.96	8.59	-
Mg^{2+}	218.94	1361.60	136.16	27.23	-
K^+	-	351.10	35.11	7.02	-
Ba^{2+}	-	0.01	-	-	-
Sr^{2+}	-	8.37	0.83	0.16	-
Cl^-	15,117.25	20,040.00	2,004.00	400.80	-
SO_4^{2-}	550.63	3,500.00	350.00	70.00	-
HCO_3^-	1,135.9	47.58	4.75	0.95	-
TDS (mg/l)	25,670.86	37,198.14	3,719.81	743.96	-
pH (adim)	8.01	7.80	7.20	6.75	7.00
Viscosity (cp)	1.03	1.07	1.00	0.99	1.00

3.1.4 Additional Chemicals

Methanol: Solvent used for the removal of water and displacement of toluene during the cleaning process in the rock samples. Methanol was purchased from VWR International, with a concentration of 99.8 %.

Toluene: Solvent used for the elimination and cleaning of organic material in the cores. It was purchased from VWR International, with a concentration of 99.5 %.

Methyl Orange: pH indicator employed in titration.

Hydrochloric acid: Utilised for titration.

3.2 CORE PREPARATION

3.2.1 Cores

A standard preparation practice was utilised, with some adaptations due to the nature of the crude oils. The method of displacement with solvents was applied because the Soxhlet extraction would probably turn out to be less effective for the cleaning of the sample. Different combinations of solvents has been proposed to restore the reservoir conditions (Cuiec, 1975; Puntervold et al., 2007; Austad et al., 2008); however, for this research the cores were previously cleaned with toluene and methanol at 60^{o} C, at an internal pressure of 500 psi, then dried at 92^{o} C and weighed.

The dried cores were saturated with formation water and different initial water saturations (Swi) were obtained. Swi of the cores ranged from 28.30 to 32.13 % and 28.12 to 36.90 %, for limestone and dolomite samples, respectively. Once the specific water saturation was established using crude oils, the cores were aged and flooded with fresh crude oil at different times for 20 days, to restore the original wetting conditions. In the brine permeability studies, some cores were fully saturated with specific brines but they did not never get to be saturated with crude oils.

3.3 METHODS

3.3.1 Contact Angle Setup

The contact angle measurements were performed by the pendant drop technique, using a Drop Shape Analysis System (DSA100) from KRUSS. It consists of the following main parts: a high speed camera which takes digital pictures at intervals of time, a light source with an integrated light blind for small contact angles, a Hamilton syringe (Gastight 1700 series) with a capacity of 500 uL, a special U-shaped needle which is positioned in an optically clear in-house holder and immersed in the brine, and the DSA4 software module that has a resolution for the contact angle of ±0.1 degree. In general, the methods used to measure the contact angle were Tangent Method 1 and Tangent Method 2.

The carbonate plates were cleaned with toluene and methanol and the slabs were dried, following the procedure applied for coreflood experiments. The slabs were then equilibrated in the formation brine at room conditions for 1 week. Two procedures were applied to the treated slides. For some plates, once the carbonates plates were equilibrated with the formation water, the excess water was removed and each plate was place inside the special holder containing the selected brine. Another group of plates were aged with crude oil at elevated temperature (92^{o} C) for 20 days. The plates were newly cleaned using toluene, to eliminate the excess of crude oil, then placed inside the holder with the brine.

As soon as the system was ready, an oil drop was released from the needle, allowing contact with the surface of the treated slide. The contact angle was observed for at least 20 hours, as the oil drop usually displays time-variant behaviour. The angle changed gradually and eventually reached a stable value. Digital pictures were taken at different intervals. These experiments were conducted at room temperature.

3.3.2 Adhesion Tests

Before the contact angle measurements, a modification of the procedure developed by Buckley et al. (1989) was performed. This simple, quick and semi-quantitative procedure was applied to evaluate if the crude oil had adhered to the slide surface. When the oil drop was generated from the U-shaped needle, it was brought into contact with the slide, which had been previously submerged in brine for a brief period of time (2 minutes). At intervals, pressure was exerted on the oil drop, to check whether the crude oil was attached at the first contact or not. Later, the needle was gently withdrawn. The results are presented in two groups, according to whether the crude oil had adhered to the slide or not.

3.3.3 Spontaneous Imbibition Tests

Seven cores were used for these tests. After aging, the cores were removed from the core holder and placed in a typical Amott Cell, using different imbibing fluids at 92^{o} C. The oil production by spontaneous imbibition was constantly monitored. The prepared cores were placed in a vertical position and surrounded by working brine. The oil production was constantly monitored. After a while, oil recovery was measured versus time. Expelled oil that was still attached to the cores was removed as much as possible, by gently shaking the cell. Once the production had stopped, the oil and brine were removed and centrifuged. Brine samples were then taken to be analyzed.

3.3.4 Forced Imbibition Tests (Coreflood Experiments)

Two hydrostatic coreholders were used for cores with diameters of one inch and two inches. The working temperature was maintained and a high overburden pressure (1500 psi) was applied along the length of the core sample (radially and axially). In addition, a back pressure (500 psi) was used to maintain the pressure of the core outlet and deliver the produced liquids at atmospheric pressure. The orientation of the cores was horizontal. Particular brines were injected into the core at a constant rate, which never exceeded 1 ft^3/day. Injection of the fluids through the cores was performed at 1 cm^3/hr for limestone cores and 2 cm^3/hr for dolomite cores. The same rates were used in all

stages of the experiments unless otherwise stated. In all of the tests, once the oil production stopped, a change of the injection rate was applied to make sure that there was no more mobile oil (between 10 and 20 cm^3/hr). Either two or sometimes three brines were considered for each of the forced tests, based on core's response to the previous injected brine.

The oil volume (expressed as a percentage of the original oil in place) was measured as a function of pore volume injected. Some tests had an additional coreflood experiment in order to evaluate repeatability of the results. These were consistent with the first measurements. Working brine and oil were first collected and centrifuged and then the separated water was analysed using routine analytic procedures. All the coreflood tests followed the same procedure to obtain similar conditions.

3.3.5 Ionic Composition Analysis

A compact ion chromatograph (883 Basic IC plus) manufactured by Metrohm, was employed to obtain the ionic concentrations of the effluents after the water injection experiments. Prior to the analysis, all the water samples were centrifuged and diluted to 1:100 using distilled water and the ion concentrations were finally calculated based on standard solutions.

3.3.6 Viscometer

A temperature-controlled viscometer (VISCOlab 3000) was used for viscosity measurements at different temperatures. The device is equipped with an integrated heater that allows precision for the viscosity readings at specific temperatures (from slightly above ambient to 180^o C). It provided an accuracy of ± 1.0 % and was suitable for the crude oils in this research.

3.3.7 Density meter

A DM 40 density meter from Mettler Toledo was employed to measure the density of the oil/water samples accurately. The instrument was able to calculate the density at temperatures between 15 and 100^o C.

3.3.8 Titration

Quantity of Water in Crude Oil Samples.- The C20 Karl Fisher titration method was applied for measuring the water content in the crude oil samples at room conditions. In all tests the measurements were corroborated to verify their accuracy and repeatability.
Amount of Bicarbonates in Water Samples.- A standard methodology for the evaluation of bicarbonate in the water samples was used at room conditions. Methyl orange was added to the water samples and the treated samples were then titrated with 0.1N hydrochloric acid. This is a simple and rapid method of determining carbonate concentration in water samples.

3.3.9 pH Measurements

Due to the variations of pH of the water samples during the experiments, a pH measurement instrument, S400 produced by Mettler Toledo, was utilised to measure the pH deviations. All the water samples were free of organic compounds from the crude oils.

CHAPTER 4 – FLUID/ROCK INTERACTIONS

INTRODUCTION

One important consideration in the selection of a water composition for EOR in carbonate reservoirs is the compatibility between the elements of each system and the injected fluids. Interaction of the injected water with the rock and native fluids may affect the natural state of the system. The details of the interactions between reservoir fluids and injected fluids or injected fluids and rock can vary widely depending on the composition of such elements. For this reason, the interactions between these elements should be meticulously evaluated before and after each experiment. Simple and practical analyses could reveal the level of complexity and at the same time improve understanding of the mechanism/s believed to underlie the good recovery factors obtained with "smart water". The complete evaluation of the fluid/rock interactions would thus lead to a better picture of such mechanisms. In this chapter, the analysis will firstly concentrate on studying the simplest interactions between the formation and injected fluids and the rock, as shown in Figure 4.1. In a series of experiments, carbonate rocks (cores), brines and crude oils were individually analysed and then systematically mixed with each other in order to gain a comprehensive understanding of their interactions. Representing three fluids and predicting their interactions with each other and subsequently with the rocks presents a problem that is not easy to solve.

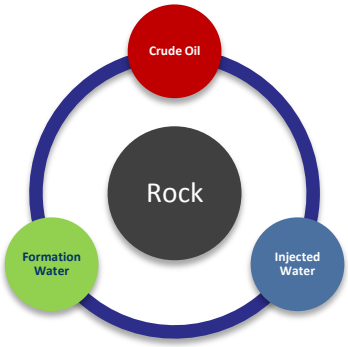

Figure 4.1: Variables dictating or affecting the original reservoir conditions.

This chapter thus includes 4 sections. In section 1, interactions between formation water and injected water will be analysed at different temperatures. The second section will cover crude oil/injected water interactions under the same conditions. Section three will be devoted to rock/injected water interactions. This section will specially focus on the presence of rock dissolution, which has been the centre of attention in the past. Both practical tests and single phase experiments were used for better comprehension of the observed effects. The last part of the chapter summarises the results obtained.

4.1 INTERACTION OF FORMATION WATER AND INJECTION WATER

Some salts show unusual behaviour and become less soluble in water as the temperature increases (Carlberg et al., 1973; Li et al., 1995). Figure 4.2 presents a documented case where seawater was mixed with formation water, resulting in salt precipitation ($CaSO_4$). The compatibility between formation brine and injected or imbibed brine was verified. The brines (FW, SW, LSSW10 and LSSW50) were prepared with specific concentrations. The ionic compositions were summarised in the previous chapter. The formation brine was mixed with each of the others with ratios from 10/90 to 90/10, respectively. The new solutions were left at either 20^o C or 92^o C for one week (Figure 4.3) for equilibration and to visually observe any changes or formation of salts. This protocol was repeated at least twice for each new solution generated. There was no precipitation under different volume fractions either at 20^o C or at 92^o C. It was concluded that the low salinity waters and seawater would not cause any precipitation in contact with the formation brine.

Figure 4.2: Salt crystal formation at high temperature.

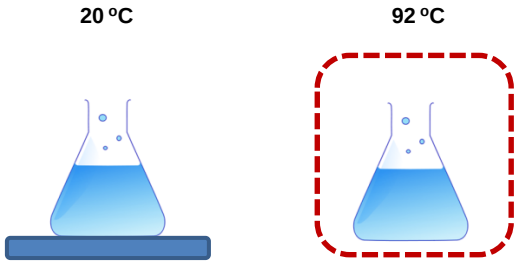

Figure 4.3: Mix of brines at different temperatures and ratios.

4.2 INTERACTION OF CRUDE OIL AND INJECTION WATER

A very similar procedure to that described by Gachuz et al. (2013) was used for this case, in which the crude oils were brought in contact with some working brines at two temperatures, 20^{o} C and 92^{o} C, as shown in Figure 4.4. Brines were prepared with different compositions. They were then brought into contact with crude oils and the samples were aged for one week at the two temperatures. The samples were periodically shaken and then both samples were left for equilibration at room temperature. Finally, the samples were centrifuged. Measurements of the basic properties for both fluids were at room conditions (20^{o} C). The crude oil showed changes in viscosity, density and water content. For instance, water content increased for each sample after the contact and the metal content of each crude oil sample also clearly showed variations in concentration, as shown in Table 4.1. Whilst LSSW10 gained much more calcium, magnesium and sodium, the use of seawater with the crude oil "A" got to some extent the mentioned metals. This would initially indicate that the water tends to be suspended in the crude oil. The water could have been then retained by two mechanisms: a) chemically by asphaltenes and resins and b) by viscous retention of water droplets (Fingas et al., 2012).

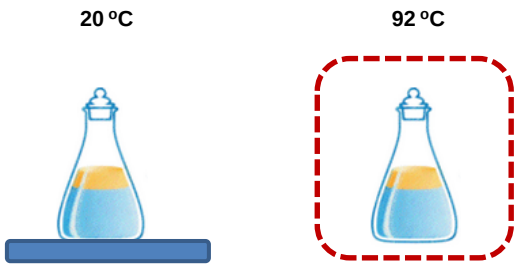

Figure 4.4: Mix of brines with crude oils at different temperatures and ratios.

Table 4.1: Water and metal content present in the crude oil samples, crude oil "A".

Crude Oil Samples	**Water Content (ppm)**	**Metal Content (mg/kg)**			
		Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}
Crude Oil "A"	208.40	5.40	0.80	0.80	9.80
Crude Oil "A" after the contact with SW	2,023.36	6.70	0.90	3.30	26.80
Crude Oil "A" after the contact with LSSW10	6,216.23	10.00	3.20	11.80	94.30

The crude oil samples were also studied using a gas chromatography-flame ionisation method for determination of carbon number distribution (CND). Examination of the analyses of crude oils indicated a relatively high variation in their internal structures, as shown in Figure 4.5. This method allows crude oil samples to be quantitatively compared with a relatively similar matrix for specific compounds. Results of % weight vs carbon number distribution for each crude oil sample were plotted from C_{30} to C_{70} (where the heavy compounds are mainly found). The CND data for $\geq C_{30}$ showed a variation of their % weights. In particular, from C_{45} to C_{70}, low salinity water turned out to be more important, indicating that there was a significant change in the crude oil after the contact: there was an increase in the values of the weight. In contrast, the values for crude oil samples in contact with seawater, remained slightly lower from C_{38} to $C_{59,}$ while from C_{61} to C_{70} their values coincided with those for the original crude oils. This clearly indicates structural changes due to brine/crude oil interactions for the heaviest compounds.

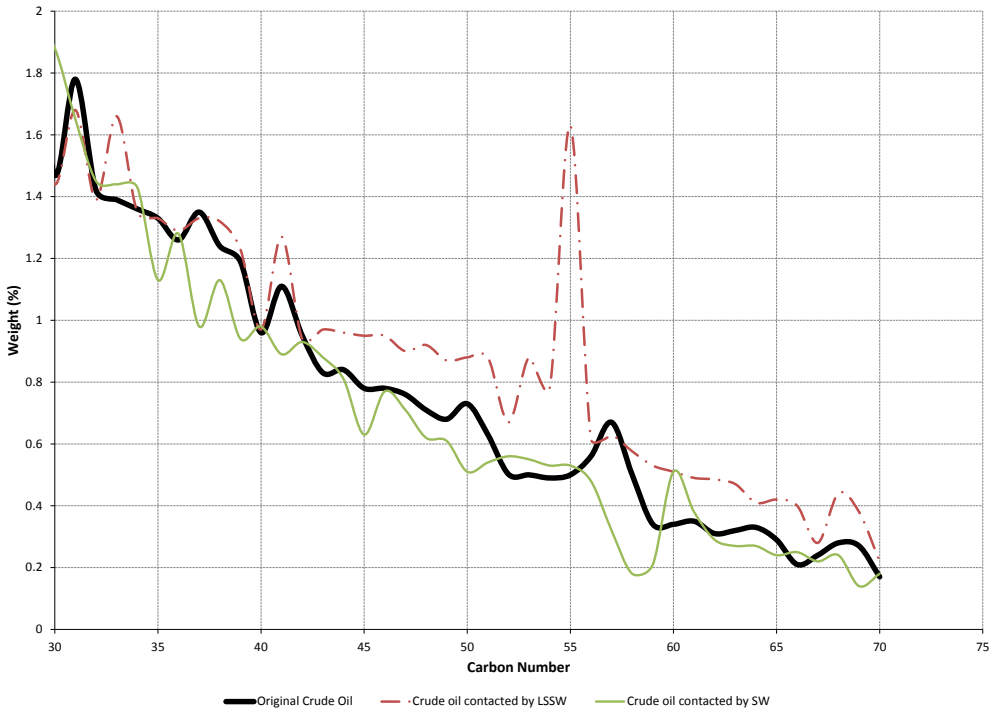

Figure 4.5: Variation of the crude oil structures after contact with water.

Alvarado et al. (2014) found that structural changes of the crude oils may occur when they are in contact with low salinity fluids. Although the results shown in Table 4.1 and the trends observed in Figure 4.5 are in line with their findings, these observations are not studied in this thesis because it is assumed that those effects (microdispersions) are more important for the flow of fluids and transport.

The analyses of the water also indicated variations of its pH, showing more acidic conditions for brines in contact with crude oils. Figure 4.6 shows the values obtained for five types of water which were left at 92^{o}C. Black cylinders represent the original values before contact with the crude oils. The pH values of the formation water did not undergo any change; they were in equilibrium with the crude oils. When salts are removed from the brines, in this case from seawater, there will be natural reactions involving the original brine and compounds found in crude oils, resulting in the formation of *new and different type of waters*. Note that the used crude oils have high total base numbers, except crude oil "E" which is more acidic.

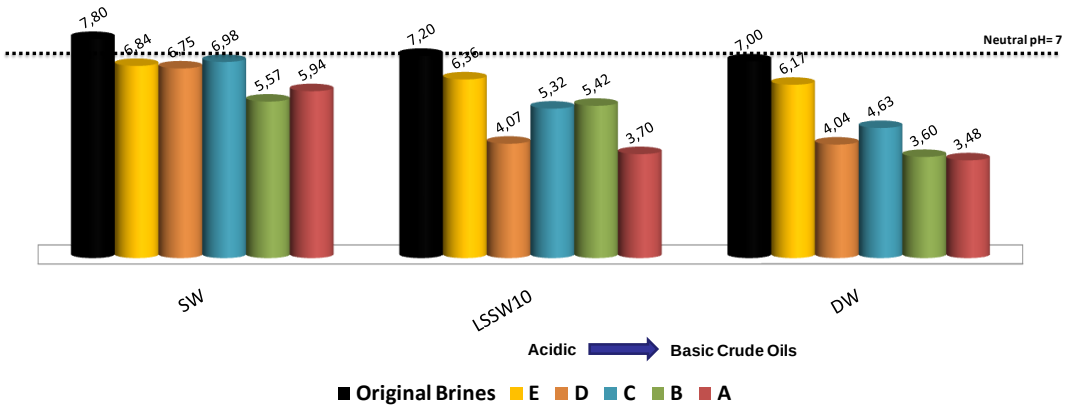

Figure 4.6: pH values for brines samples after the contact with crude oils.

Considering these preliminary results, a new set of experiments was developed under static condition where fluids, crude oils and working brines were all in contact at the same temperatures. Let us take two crude oils, one acidic and one more basic. The results are rather similar, as can be seen in Figure 4.7. When crude oils and diluted brines (LSSW10) were shaken together, the pH values did not vary significantly (from 3.59 to 3.70 at 20 and 92^{o} C, respectively). When the fluids were not shaken, once again, the pH values did not change (from 3.92 to 3.98 at 20 and 92^{o} C, respectively). Although this simple evaluation revealed a pattern in the results, it is presumed that temperature could have not had a large effect on the interactions between crude oil and brine, even when the fluids were in static conditions. This would mean that there is a natural interaction between injected waters and crude oil leading to a transfer of certain compounds, independently of the movement of the fluids. This was not very noticeable when high salinity water (seawater) was in contact with specific crude oils in the earlier experiments. However, although the transfer of water-soluble compounds migration occurs, it is not as important as when salts are eliminated from brines. Basic crude oils are playing an important role at this point.

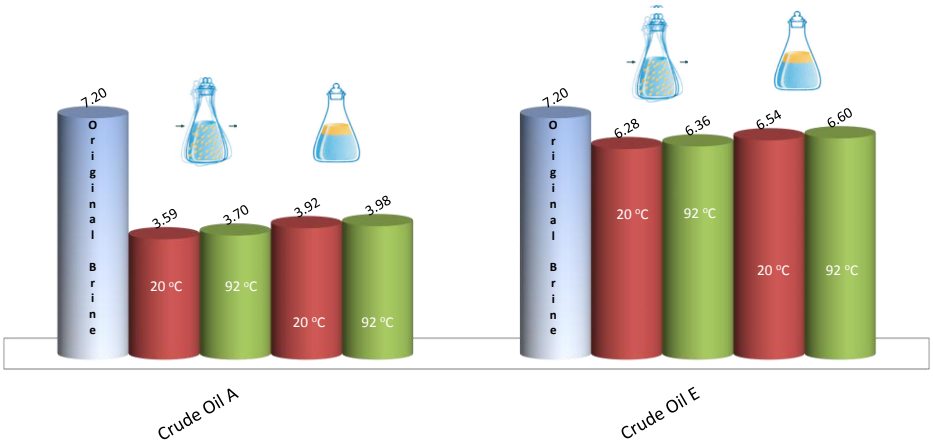

Figure 4.7: pH values for brine samples after contact with crude oils at different conditions and temperatures.

Nasralla et al. (2011 and 2014) revealed similar variations of the pH behaviour in their experimental work, but they were not able to associate such findings with the purpose of their work, which was to study the effect of the pH on the electrical charges. In 2014, they conducted experiments with a high total base number and presented the results for six brines in contact with this crude oil. Three pH values dropped a little, seawater brine kept its value almost constant and the pH of two brines was lowered from their original values.

4.2.1 Reactions Influencing the pH Variation of the Injected Water

To understand how new types of water could be formed, it is necessary to know how the crude oil interacts with water. Water is a highly structured liquid with ions and an extensive network of hydrogen bonds (Marcus, 2007). The type of ions is an important aspect, as they can either decrease or increase the solubility of organic materials in the water. Collins and Washabaugh (1984) described the terms "structure makers and breakers" in a biophysical context. Nevertheless, the use of these concepts has been accepted and utilised in a diversity of scientific fields where water is studied. Marcus organised the ions according to their effects on the water structure. In this work, the ions

related to the common effects on formation water, injected water and crude oils by metal and non-metal compounds will be considered:

- Breaking ions (chaotropes): I^-, Br^-, K^+, Rb^+, Cs^+, Cl^-, N_3^-, S^{2-}, Se^{2-}, Ra^{2+}

- Borderline Ions: Na^+, Ag^+, Ba^{2+}, Pb^{2+}, F^-, HCO_3^-

- Making ions (kosmotropes): Li^+, Cu^+, Au^+, Sr^{2+}, Al^{3+}, Cr^{3+}, OH^-, Ca^{2+}, CO_3^+, Pu^{4+}, V^{2+}, Cr^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, V^{3+}, Fe^{3+}, Mg^{2+}, CO^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}

When a significant amount of salts is dispersed in a liquid, they will considerably affect the solubility of a gas or another liquid in that solvent. If this solubility is less than that in salt-free water, this occurrence is called the "salting-out effect" (Prausnitz et al., 1999). If the solubility increases with the reduction of salt concentrations, then the phenomenon is called the *"salting-in effect*". This description is very basic because it overlooks the role of the ions. However, ions, either kosmotropes or chaotropes, like to undertake important reactions with water, thereby leaving fewer free water molecules. The kosmotropic solutes are ions with small radius and high surface charge density. Calcium and magnesium are good examples of strong kosmotropes. The chaotropic solutes are longer ions with smaller surface charge density. For instance, this would indicate that calcium and magnesium will reduce the solubility of other solutes and chloride or sodium would help to extend the solubility of these solutes, such as water-soluble fractions from crude oils.

On the other hand, the crude oils are very complex mixtures of hydrocarbons and can be different from one reservoir to another, and many of these are inadequately characterised, due to their attributes. Crude oils may be classified based on their chemical structures or physical properties. The latter are much easier to measure than are chemical structures (McCain, 1990). Hughey et al. (2002) identified around 11,000 individual compounds in one crude oil, but their individual detection is hard, which is why the identification of hydrocarbon groups is more commonly employed.

The hydrocarbons in crude oils which contain only hydrogen and carbon can be divided into two main groups: a) aliphatic (alkanes, alkenes, alkynes and cyclialiphatics) and b)

aromatics. It should be recalled that hydrocarbons such as alkanes, alkenes and aromatics are "water insoluble" because they have non-polar fractions. There are many other organic compounds, which contain nitrogen, oxygen and sulphur (McCain, 1990). Crude oils also contain appreciable amounts of such organic non-hydrocarbon compounds with sulphur, nitrogen and oxygen (these combine with long ring structures to form resins and asphaltenes) and in smaller quantities, metal components in solution and inorganic salts in colloidal suspension. Even though the concentrations of compounds such as carbon dioxide or hydrogen sulphide in certain fractions may be quite small, their influence is important in other crude oils, especially in heavy crude oils.

A simpler criterion can be to arbitrarily group crude oils with similar characteristics, for example, into four general fractions: saturates, aromatics, resins and asphaltenes (SARA technique). Resins and asphaltenes are considered as the most active compounds in crude oils because they contain polar components. These components have fractions with basic and acidic functionalities. Nitrogen compounds are the main fractions of basic components in crude oils and generally fall within the range of 0.1 to 0.9 %, although they may represent up to 3 %.

The asphaltenes group contains large molecules and which are less water-soluble. Resins have smaller molecules and contain acids and bases that are more water-soluble. Acidic crude oil components, sometimes termed as naphthenic acids (RCOOH), exhibit activity and are part of resin fractions. The naphthenic acids' total content in crude oils is commonly determined by potentiometric titration and expressed as Total Acid Number (TAN). The smallest molecular weight acids are dissolved in the aqueous phase, whilst the larger naphthenic acid molecules are oil-soluble. However, some of them may be water-soluble at high pH (Rudin et al., 1992; Sjoblom et al., 2000). Naphthenic acid frequently describes all carboxylic acids present in crude oils and when they have three rings they are said to be more hydrophilic (water-loving) than acids with one or two rings (Havre et al., 2003). Water-solubility is related to pK_a ($pH>pK_a$, negatively charged molecule) and pK_b ($pH<pK_b$, positively charged molecule is created), relating to the acid and base respectively. The strength of an acid (pK_a) denotes the tendency of a molecule to give up or remove a proton to water at a specific pH. Most carboxylic acids have a pK_a, between 3 and 5. Moreover, all carboxylic acids,

whether insoluble or soluble in water, react in the presence of NaOH or KOH and other strong bases to form salts. Naphthenic acids also contribute to the formation of emulsions and soaps (in enhanced oil recovery), affecting the surface tension between reservoir fluids and alkaline solutions (Odberg, 1985; Marquez, 1999; Acevedo et al., 1999; Rogers, 2002).

A good example of this reaction between water and crude oil is the injection of surfactants to the reservoirs. Alkali injection is a process in which water is injected into the reservoirs at an elevated pH (10 to 12) value to improve oil recovery. The effect of the water prepared with chemical compounds is partially due to the chemical reaction between this added product and organic acids that are found in the crude oils. If the (alkaline) aqueous phase is in contact with the crude oil, there is a reaction which can form surfactants (soaps) and emulsification. Consequently, the capillary pressure between the oil phase and the injected solution may be reduced, producing a lower interfacial tension (IFT), and hence allowing displacement of the residual oil towards the producing wells. McGuire et al. (2005) propose that low salinity water and alkaline injection act in a similar way.

At reservoir conditions, the pH of the formation water is around 5-8, so the majority of the water-soluble acids (85 %) are expected to be dissolved in the water, but their dissolution will also depend on the composition of the reservoir water (Reinsel et al., 1994). In general, if the pH of the solution is 2 units higher than the pKa, then the acid will be nearly 100 % ionized. This fact determines that the carboxylic acids are either diffused in an aqueous solution or better placed in relation to the crude oil/water interface. In this way, each carboxylic acid will be present totally as its anion, at the crude oil/water interface (reaction 4.1).

$$RCOOH + H_2O \Leftrightarrow RCOO^- + H_3O^+ \qquad 4.1$$

As the H^+ concentration is higher in such aqueous solutions, the pH will be lower, creating a very acidic environment. Therefore, in the current experiments, the reactions of migration of the acidic components (salting-in effect), when crude oils and water were in contact, were mainly controlled by the composition of the water and its pH. As the pH of the injected brine exceeded the pKa for the acid compounds from the crude

oil, the acids and water-soluble compounds, tended to dissociate and change into negatively charged molecules. For this reason, as shown in Figure 4.6, such acidic compounds became more water-soluble and active in both low salinity (LSSW10) and pure water (DW), except for seawater which turned out to be only important for the crude oils "A" and "B". As a result, the presence of polar compounds creates *acidic waters* which may dissolve the carbonated rock. Crude oils with low TAN were especially prone to create such acidic waters (Figure 4.6). The reason for the higher pH of the crude oil "E" after contact is that it has the lowest amount of water-soluble acidic compounds. Therefore, Crude oil "E" may contain larger acid molecules (oil-soluble components) than the other crude oils. The *acidic water* created by oil/ injected water interaction is practically impossible to detect or observe, even in laboratory experiments, because the effluents (produced water from experiments) give high pH values. This phenomenon is just perceptible when crude oil is in contact with injected waters.

Since carbonate has a positive charge, the acidic compounds (oil-soluble acids) in heavy crude oils should be adsorbed in the rock because heavy oils contain higher volumes of both resins and asphaltenes. The natural state of wettability should then be mixed or oil wet, which is in line with several studies that have reported contact angle measurements indicating that carbonate reservoirs are usually more oil wet than reservoirs with silica (Chilingar et al., 1983; Treiber et al., 1972). As the reservoir fluids and rock are, to the best of the researcher's knowledge, in equilibrium, we may assume that:

1.- Under high salinity water injection (formation water), the salting-in effect is not important, because the crude oil/formation water/rock system keeps its balance and stability, except for specific crude oils where a drop of pH is observed, as shown in Figure 4.8a. In general, high salinity water tends to remain closely associated with the rock and reservoir fluids, preserving an equilibrium state.

2.- If a low salinity fluid is injected, there will be a transition zone in which this water is mixed with formation brine, generating new water with different characteristics. Although that generated water may contain fewer ions, the crude oil compounds will barely diffuse (Figure 4.8b). This is especially important because the different concentrations between the formation water and the injected water will contribute less

to the oil recovery. In Figures 4.8a and 4.8b, it can be seen that the rock/water and crude oil/water interfaces are still in equilibrium and they are negatively charged at high pH. According to some authors (Healy and al., 1978; Buckley and al., 1989, Dubey and Doe, 1993 and Jada and Salou, 2002), the electrical properties may change as a function of the pH and the composition of the injected fluid and the crude oil, suggesting changes at both interfaces.

3.- Subsequently, when the area has been completely invaded by low salinity water, the loss of ions causes a collapse in the system (at this point, according to Le Chatelier's principle, the system has to be re-established) and leads to better dissociation of the acidic compounds, which may migrate or be diffused into the current water or reside at the crude oil/water interface (*salting-in mechanism*), Figure 4.8c. The low salinity water or pure water associated with more hydrogen ions will then act as *acidic water (new water begins forming)*. The system therefore has to compensate the crude oil compounds for the loss of hydrogen ions. The hydrogen ions may be replaced by other reactive ions of metals such as magnesium, calcium, potassium or sodium, so the water-soluble compounds again undergo an association process. This is in good agreement with the results in Table 4.1. Usually, potassium, sodium, calcium and magnesium react with water and acids, and are regarded as more reactive than the hydrogen ion.

Moreover, many studies have postulated that the rock/brine and crude oil/brine interfaces will be positively charged because of the low pH value (Healy and al., 1978; Buckley and al., 1989, Dubey and Doe, 1993 and Jada and Salou, 2002). Due to the presence of two interfaces with the same positive charges, a natural electrostatic force of repulsion will occur between rock/brine and crude oil/brine interfaces (Dubey and Doe, 1993) and the rock surface will then release the crude oil drops (*change of wettability*) which tend to mainly be ionised by positive ions, Figure 4.8c. The crude oil/water interface captures more positive ions such as calcium and magnesium, contributing to the formation of stable and strong regions around the crude oil drops.

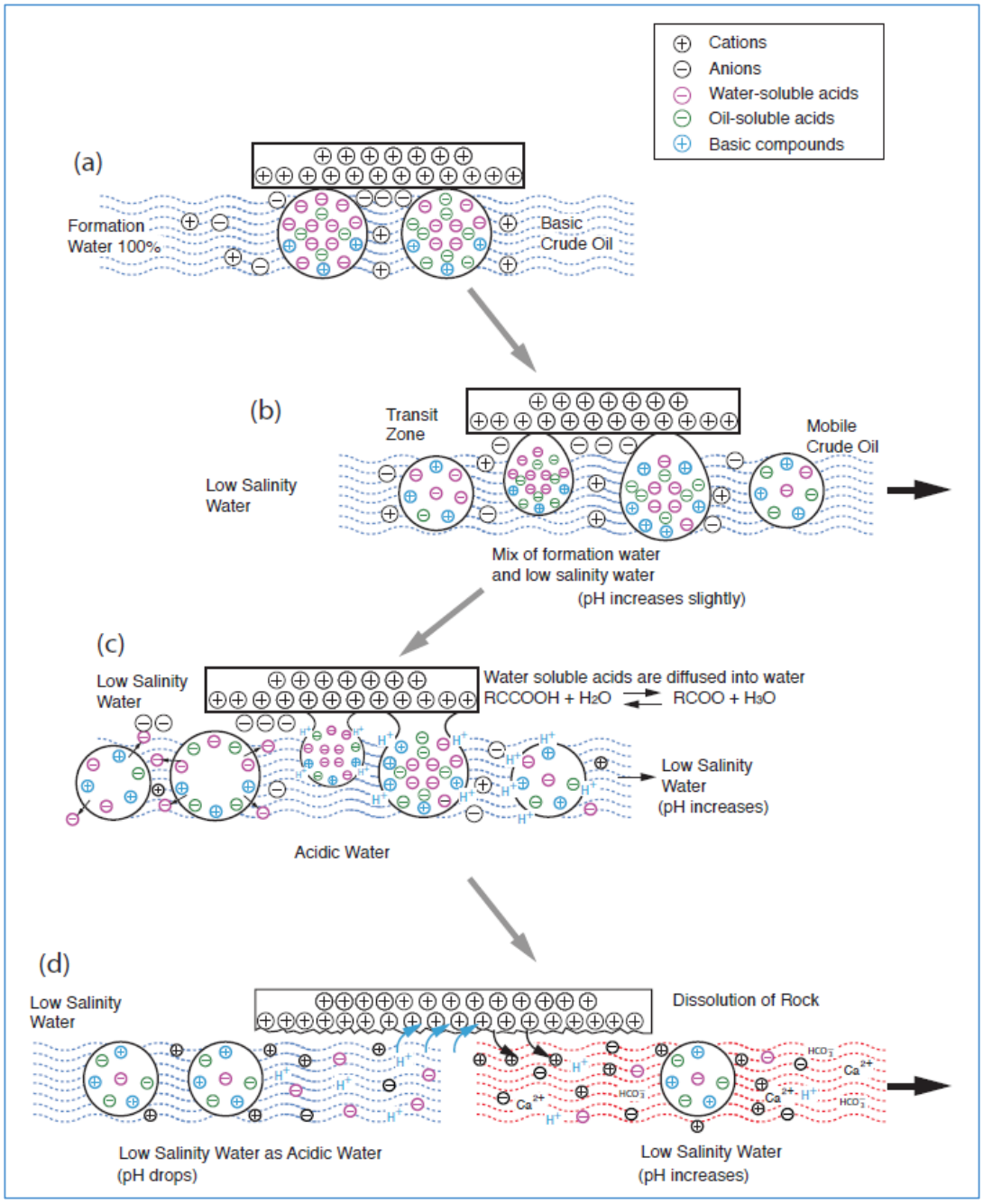

Figure 4.8: Sequence of effects in a system that is under injection with low salinity water.

4.- As the carbonated formation is being exposed to the aggressive action of this *acidic water*, the *rock dissolution mechanism* will immediately take place where the crude oil has been released and in areas exposed to direct contact with formation water (Figure 4.8d). As soon as *rock dissolution* occurs, the pH of this *acidic water* will increase gradually and be adjusted because ions (bicarbonates) are being liberated from the rock.

The produced water will probably be a mixture of dissolved hydrocarbons, additional amounts of ions from the rock and existing ion concentrations in the formation and injected water. Additionally, the crude oil drops could suffer internal modifications such as changes of their structure, viscosity and density variations or disparities in their amount of water. These assumptions are also in line with the findings shown in Table 4.1 and the Figure 4.5, presented above. Recent studies have given an idea about the structural changes of crude oils brought about by contact with low salinity fluids, thus opening a debate regarding a new mechanism for smart water (Gachuz et al., 2013; Alvarado et al., 2014).

5.- Finally, at some point, *the natural generation of acidic water* will decline, due to the absence of crude oil and the pH from the produced water should become higher but more constant.

Based on this reasoning, *generation of acidic water* may be responsible for part of the low salinity water effects observed in carbonate rocks. Thus, it is plausible to believe that more than two mechanisms can simultaneously occur in low salinity water injection for these types of formations. The *generation in-situ of* these types of *acidic waters* will depend on the amount of crude oil present in the cores or maybe even in the reservoirs. It also depends on the presence of hydrogen concentrations that are transferred to the waters. The model in Figure 4.8 supports the assumption that basic crude oils were susceptible to donating hydrogens ions in the cases analysed. For the acidic crude oil examined, the migration was minimal, resulting in an absence of acidic water and thus an unimportant amount of rock dissolution. To support these conjectures, the next sections will provide evidence with regard to the phenomena of dissolution and formation water/rock/crude oil/injected water interaction.

Nevertheless, one cannot generalise that the proposed model is applicable to all basic crude oils or unsuitable for all acidic crude oils. The components of oils dictate what kind of interactions will occur in oil reservoirs. In many cases, oil and gas reservoirs contain non-hydrocarbon constituents, such as carbon dioxide, nitrogen or hydrogen sulphide (McCain, 1990). Some of these can be soluble in the reservoir water and can also influence an adjustment of the pH. For instance, a decrease in salinity of the water improves the solubility of carbon dioxide (CO_2), causing a lower pH (Klins, 1984)

under certain pressure and temperature conditions. When CO_2 is dissolved in water, a small proportion of it reacts chemically with this water to make carbonic acid, H_2CO_3. This, likewise, causes the possibility of producing dissolution from the carbonated rock. As can be seen, the synergy between crude oils and injected waters is likely to be greater than other interactions.

4.3 ROCK/ INJECTION WATER INTERACTION

The process of solid precipitation of salts is not limited to water/water interactions; it can also be caused by incompatibility between injected water and rock mineralogy. The precipitation may reduce the permeability considerably; therefore, injectivity may be reduced. Before running an experiment, selected cores (limestone and dolomite cores) were first fully saturated with formation brine. Then the brine permeability of each core was obtained. Later, the cores were cleaned with toluene and methanol and then once again they were saturated with either seawater or low salinity brine and permeability was measured. In general, there were no changes in the cores' permeability. The variations were not significant. The results established that working brines would not cause any major damage to the rock. The effluent samples were analysed for all ions and some results are presented in Figure 4.9. The solid lines are the original concentrations in the prepared brine.

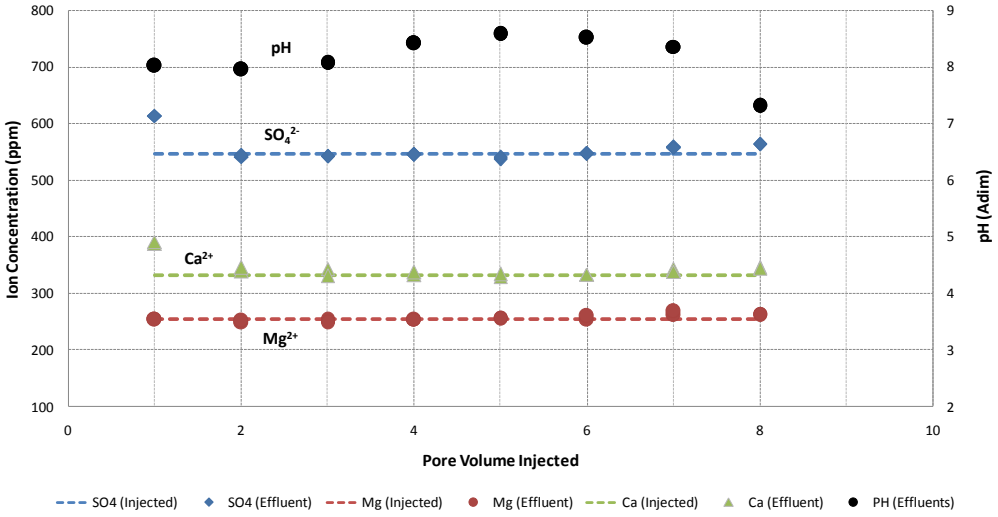

Figure 4.9: Concentrations of certain ions in the effluents at specific pore volumes.

The analyses of the effluents revealed that some ions were released, including sulphate and small amounts of chloride and sodium. Although the mineralogy analyses did not show occurrence of SO_4^{2-} beforehand, analysis of effluent water samples detected these concentrations. This indicated that the source of these ions was dissolution or release from the rock surface. Later, it was confirmed that all the cores had traces of anhydrite.

The pH of various effluents was also analysed. The pH of the produced water for the cores when they were saturated with formation water remained close to 8.0, indicating a "chemical equilibrium" between the injected formation water and the core surface. The change in the pH is presumably due to the effect of bicarbonate and calcium from the rock. When the brine permeability was measured with formation water, some cores were newly saturated with formation water without bicarbonate, pH= 6.3. For these cases, the pH from the effluents rose to ~ 7.12 (limestone cores). Similar results were obtained for dolomite cores, from an initial value of ~6.3 to ~7.6, also saturated with formation brine without bicarbonate. As we know, the pH of a solution can change. Certain factors can affect its value, such as ionic strength of solution or temperature changes. There are also some chemicals that can raise or lower the pH. Lime, sodium bicarbonate, calcium hypochlorite, sodium hydroxide, sodium hypochlorite or others can increase the pH of the solution. Sulphuric acid and carbon dioxide are examples of chemicals which decrease pH.

McGuire et al. (2005) proposed that the increase in pH could be an indication of the low salinity water effects. They linked this research with alkaline injection for enhanced oil recovery. However, one year later, Lager et al. (2006) reported that more oil production had been obtained without a rise in the pH. Zhang et al. (2008) also ruled out this effect, arguing that there was no relationship found between oil recovery and effluent pH in their experiments. Austad and colleagues (2010) offered a description based on the detachment of adsorbed cations in the cores. According to their explanation, the low salinity water injection caused desorption, promoting the substitution of a calcium ion by a hydrogen ion. Gamage and Thyne (2011) considered the change in pH as a reaction but not as a mechanism. Thus, the results of this section supplement these earlier findings, where the jump in the pH values is a result of material released from the cores

independently of the interaction achieved between formation water and the rock surface or injected water with the same rock

4.3.1 Occurrence of Dissolution in Carbonate Formations

The dissolution effect was first proposed by Hiorth et al. (2008). They took experimental work from the Austad research group (2002, 2005, 2008, 2009) for the creation of a geochemical thermodynamic model. Chalk dissolution was suggested as the mechanism for the wettability change. Many other authors have reported the possible presence of this mechanism, but the reasons by which it occurs are currently an unsettled issue. Data as direct evidence of this phenomenon has been obtained during coreflood experiments. Perhaps the most surprising fact regarding mineral dissolution is that, despite the immense importance of permeability variation, there is no strong proof of its existence.

Yousef and et al. (2010-2012) have written extensively on carbonates. They also studied the occurrence of this mechanism using NMR studies for their cores; however, they imply that mineral dissolution could occur during low salinity seawater injection. The work of Zahid et al. (2012) had suggested that the dissolution of the rock could have been a mechanism for the improvement of oil production. They considered that the additional production of calcium was a possible indication of this. Nasralla et al. (2014) assessed the potential of calcite dissolution using a geochemical model for low salinity water injection. Later, their experimental results confirmed that the calcite dissolution was not a dominant mechanism in low salinity water injection. These assumptions and others are not surprising, considering that their conclusions are based on inaccurate measurements of this event during coreflood experiments. Absence of pressure variation in the differential pressure (ΔP) analysis throughout their experiments (Nasralla et al., 2014 and Al-Hasim et al., 2015) caused the misinterpretation this phenomenon. It is rather difficult on the basis of the data obtained from some of the mentioned experiments to ascertain the presence or absence of this phenomenon.

In order to understand the issue of interest, mineral dissolution, we should first determine if such a reaction is really participating in the rock/fluid interactions. One preliminary way to elucidate it is to use a geochemical modelling program capable of

simulating or predicting a wide range of chemical reactions between rock and water. In the next phase of this research, PHREEQC (Appelo and Postman, 2005) was employed as an explanation instrument to predict possible reactions between the rock and the injected water. Later, single phase tests in limestones cores were run in order to analyse the influence of the water when in contact with crude oils.

4.3.1.1 Geochemical Calculations

PHREEQC is a geochemical modelling program designed by the United States Geological Survey (USGS). The program is useful for different fluid/rock interactions and PHREEQC works reasonably well in sodium chloride solutions like seawater or with low salinity concentrations. For this reason, some functionalities offered by this simulator were utilised here. The phase equilibrium option was run for five brines, SW (pH= 7.80), LSSW10 (pH= 7.20), LSSW50 (pH=6.75) and low salinity water which had previously been in contact with two crude oils (LSSWCCOA and LSSWCCOE with pH~3.70 and pH~6.36, respectively). These last ones were artificially generated by bringing a volume of LSSW10 into contact with crude oil "A" and crude oil "E", which is reported to generate more aggressively acidic water than using unaltered original water. After the contact, the new waters (LSSW10CCOA and LSSW10CCOE) were separated and filtered. As the carbonate rocks are principally composed of calcium magnesium carbonate and calcium carbonate, with minor amounts of silica, clay minerals, anhydrite and gypsum, the minerals analysed were calcite and dolomite. The systems considered were closed systems, where only the brine and the given minerals were in contact.

The Saturation Index (SI) can be a relatively simple way of quantifying if a particular mineral may thermodynamically dissolve or precipitate under certain conditions. The negative Saturation Index values shown in Table 4.2 indicate a possible dissolution of these mineral samples (brine is undersaturated with respect to the mineral), especially with the LSSWCCOA and LSSW50 brines. Although PHREEQC uses either the Davis expression or Truesdell-Jones expression (another extended Debye-Hückel equation), which have been found to be accurate at low ionic strengths (Langmuir, 1997 and Parkhurst and Appelo, 1999), the Pitzer model (Pitzer et al., 1973, 1974 and 1975) was also applied for those cases, with the intention of estimating its future usefulness . This

last equation (the Pitzer equation) has been widely accepted to model the thermodynamic properties of high ionic strength waters; however, the Pitzer expression, was also found to be a good choice for modelling this group of waters, as shown in Table 4.2. Note the difference in values of seawater and the rest of the brines. The positive index shows that the seawater will tend to precipitate a specific mineral. The mineral will only precipitate if the solution is supersaturated (SI>0) otherwise nothing happens. Temperature appears to play an important role for the seawater case where, for the calcite at 25^{o} C, the value is negative but at 50^{o} C, the mineral may precipitate. In contrast, with dolomite the seawater will be likely to precipitate more as the temperature increases with dolomite. The dissolution of the dolomite is faster than that of calcite for these brines.

Table 4.2: Saturation Index calculated for two minerals (solid species) in contact with different types of injection water.

	PHREEQC	**PITZER**	**PHREEQC**	**PITZER**
Temperature	25 ºC		50 ºC	
Brine	**Calcite**			
SW	-0.17	-0.23	0.07	0.04
LSSW10	-2.25	-2.34	-1.95	-2.04
LSSWCCOA	-5.01	-5.09	-4.68	-4.75
LSSWCCOB	-3.08	-3.17	-2.77	-2.86
LSSW50	-4.10	-4.18	-3.78	-3.86
Brine	**Dolomite**			
SW	0.55	0.57	1.18	1.28
LSSW10	-3.64	-3.67	-2.89	-2.90
LSSWCCOA	-9.17	-9.17	-8.35	-8.32
LSSWCCOB	-5.31	-5.34	-4.53	-4.55
LSSW50	-7.34	-7.70	-6.55	-6.56

Additionally, some results were obtained for the possible amount of precipitated or dissolved material, expressed in terms of mass, and the corresponding pH values of the brines were also determined (Table 4.3). Here, the second and fourth columns are relevant. In the closed systems, the dissolved amounts are expected to be unimportant, excluding the low salinity water contacted by crude oil "A", which is more aggressive. Based on the PHREEQC simulations, the pHs would be all higher, with exception of

that of seawater, which is about 0.2 units higher at 25^{o} C. These results imply that dissolution at pH ≤ 6.5 is higher compared to that at pH ≥ 6.5.

Table 4.3: Dissolved amount of minerals using PHREEQC at 25^{o} C (except for SW*).

	Moles in Assemblage	**Mass (grams)**	**pH (initial)**	**pH (Final)**
Brine	**Calcite**			
SW	-1.933×10^{-05}	0.002	7.80	7.96
LSSW10	-8.81×10^{-05}	0.009	7.20	9.19
LSSWCCOA	-1.016×10^{-02}	1.070	3.70	6.09
LSSWCCOE	-1.231×10^{-04}	0.012	6.36	8.95
Brine	**Dolomite**			
SW*	1.296×10^{-05}	0.001	7.80	7.44
LSSW10	-2.106×10^{-05}	0.002	7.20	8.86
LSSWCCOA	-5.372×10^{-03}	0.537	3.70	6.13
LSSWCCOE	-4.305×10^{-05}	0.004	6.36	8.58

At the same time, the calcium, magnesium and bicarbonate concentrations in the brines were obtained before and after the interaction with the minerals. The graphs in Figure 4.10 and Figure 4.11 depict the simulated results for calcite and dolomite. As we can see, the major change in the brines' composition is that they now have higher Ca^{2+}, Mg^{2+} and HCO_3^- values, where the original concentrations were about 42.96, 136.16 and 4.75 ppm (or mg/L), respectively. The main reason for the increase in HCO_3^- is that the program calculates the concentrations of this ion based on the initial pH. The modification in the initial conditions (manipulated pH) changes the concentration of these sensitive species. These species are now present in the LSSWCCOA in higher concentrations, although they were lower before reaction with calcite and dolomite, as described. In this case, the added amount of bicarbonate in the solution, from 4.7 to 1,150 ppm (calcite), could be increasing the pH of this particular brine (from 3.7 to 6.09), but it is not clear why the variation of their pH values occurs for the other brines, because the dissolved amount is minimal.

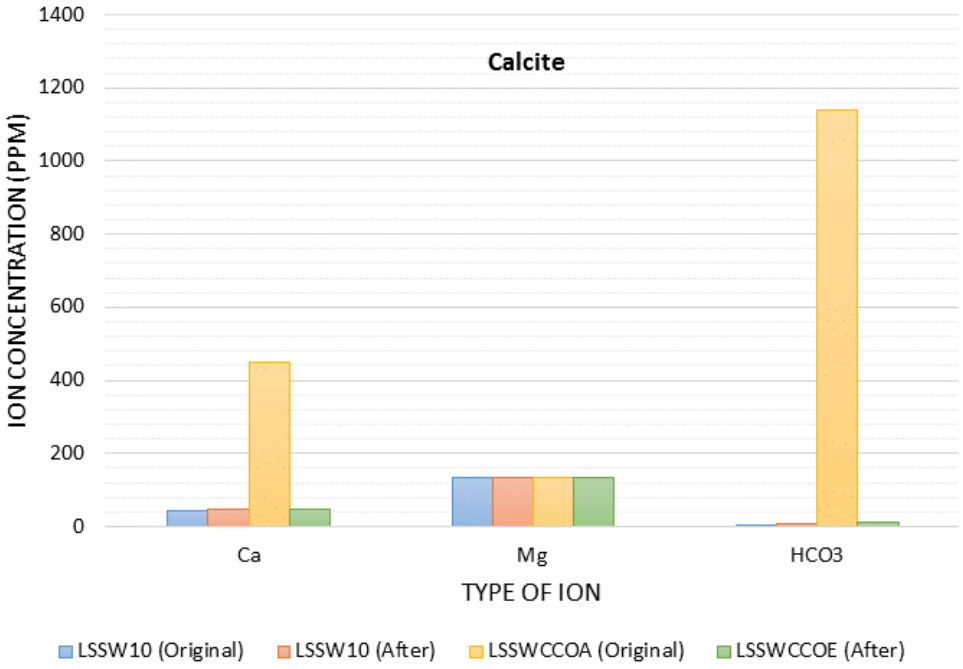

Figure 4.10: Calculated concentrations for calcium, magnesium and carbonate after interaction with calcite.

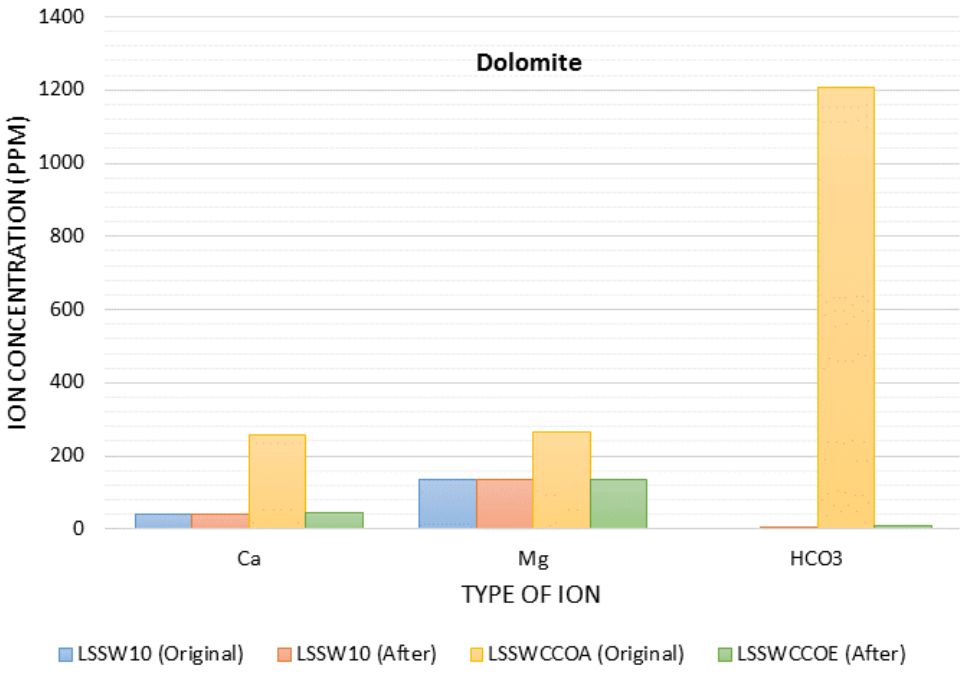

Figure 4.11: Calculated concentrations for calcium, magnesium and carbonate after interaction with dolomite.

4.3.1.2 Estimations of the Occurrence of Dissolution under Static Conditions

In theory, as mentioned and described above, dissolution may occur where there is no movement of fluids. For the PHREEQC calculations, pH and ionic concentrations of the solutions naturally increased during the contact between rocks and fluids and under no-flow conditions. To confirm the effect of the possible dissolution, a second step should involve tests when this effect could be observed under static conditions, as PHREEQC assessed the potential for dissolution using different waters. The problem of representing a system which involves 3 fluids; crude oil, formation water and fluid of injection, or predicting their interactions with each other and with the rock, is that sometimes particular assumptions are or should be taken into account.

The approach to this difficulty can be simplified by showing how they can act under static conditions, assuming a coreflood experiment, and events at specific times. Figure 4.12 is intended to exemplify this sequence: (a) at the start of the injection, when formation fluids and rock are still in equilibrium; (b) when the injection of water begins. (in fact, this period cannot be represented for these experiments, because the system has not changed); (c) later, when the core contains equal volumes of formation water, crude oil and injected water, and finally (d) when it is assumed that the formation water has been completely displaced from the core and that there are only residual oil and water of injection. To establish these relationships between such elements, a number of practical experiments were devised to meet this need.

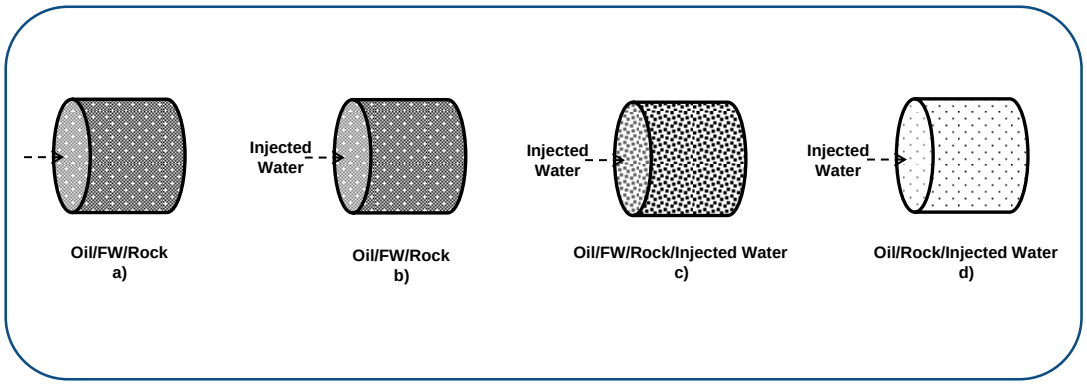

Figure 4.12: Sequence representing a coreflood experiment at static conditions, a) system in equilibrium, b) System before the injection (in equilibrium), c) System with equal volumes of fluids, d) System with residual oil and fluid of injection.

The tests evaluate pH alteration and ionic concentration changes for given crude oil/ brine/rock combinations, Figure 4.13. Tests were conducted at static conditions and high temperature. First, 250 ml glass bottles containing 100 ml of formation water, a mix of formation water/injected water and injected water (LSSW10), respectively, were left for one week at high temperature. After this period, these brines were cooled down and their pH measured. A previously cleaned fragment of rock was then added to each glass bottle and equilibrated for one week more. Next, the glass bottles were withdrawn from the oven, and a water sample was taken for IC analysis and pH values were measured again. Then, a crude oil (crude oil "A" and crude oil "E", which exhibited a change in contact with low salinity water, see Figure 4.6) was added to the bottles and equilibration was allowed. Once the glass bottles were removed from the oven, a sample of water was taken with special needle syringes and filtered; the fluids were later collected and centrifuged to fully separate the crude oils and brines. Finally, measurements of pH and ion concentration were taken. The measurements of the values were performed at room temperature.

The procedure was repeated twice and verified by comparisons between static and dynamic conditions. Dynamic conditions were produced by applying mechanical agitation to the bottles containing the samples for some minutes.

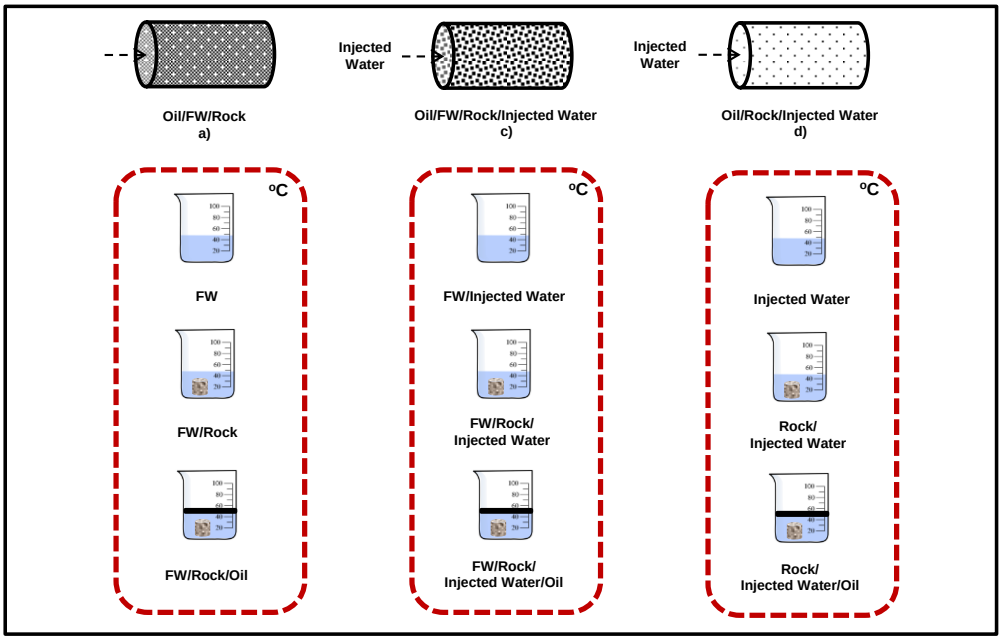

Figure 4.13: Procedure for evaluating changes in the composition of the fluids and pH values. Interactions among fluids and rock under static conditions.

A brief analysis of the effect of pH was performed to determine if crude oil/injected water interactions are relevant. The progression between the initial pH of the brines in equilibrium and the final pH of the aqueous phase after the equilibrium with the rock and the crude oil for each system is shown in Table 4.4. From the Table, it is evident that the pH is progressing when is in contact with the rock but once the crude oil arrives, the pH declines. For systems (a) and (c), the change is sometimes small but a perceptible decrease in the pH of system (d) is particularly observed for the dolomite rocks. A most significant decrease in the pH for this rock indicates a surface which is less active. By definition, dolomite is chemically less active than its limestone counterpart. The pH of the systems with the crude oils is around 7.45 and 7.30 for limestone and between 6.5 and 6.9 for dolomite. This drop is perhaps explained by the fact that the crude oil compounds interact with the aqueous solution in a different way.

Table 4.4: Behaviour of the pH for each tested system.

	Oil/FW /Rock	**Oil/FW/ Rock/IW**	**Oil/Rock /IW**
Systems with Crude Oil "A"	**Limestone**		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.39	7.99	8.16
Brine (s)/Rock/Crude Oil	7.93	7.87	7.46
Brine(s)/Crude Oil*	8.02	8.01	3.70
	Dolomite		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.50	8.05	7.50
Brine (s)/Rock/Crude Oil	8.10	7.97	6.55
Brine(s)/Crude Oil*	8.02	8.01	3.70
System with Crude Oil "E"	**Limestone**		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.39	7.99	8.16
Brine (s)/Rock/Crude Oil	7.76	7.74	7.34
Brine(s)/Crude Oil*	7.98	7.85	6.36
	Dolomite		
Brine	8.01	7.75	7.20
Brine (s)/Rock	8.50	8.05	7.96
Brine (s)/Rock/Crude Oil	7.74	7.72	6.85
Brine(s)/Crude Oil*	7.98	7.85	6.36

*Previously analysed.

The dissolution of the rock is more aggressive for limestone, implying more dissolution, as previously described above. Therefore, the limestone surface releases more material, which leads to higher pH values in comparison to the dolomite surfaces, where the capacity for dissolution is limited (Table 4.3). The low pH value of the brine (3.7) for crude oil "A" is linked to the presence of an acidic water, indicating that there is a stronger influence of the water-soluble compounds from crude oil "A" in these systems.

The impact of the crude oil in all the systems is shown in Figure 4.14. The pH values for the phases in equilibrium and the systems affected by an invading phase (Mix of brines/Crude Oil/Rock) stay constant. In contrast, from the second system (Mix of brines/Crude Oil/Rock) to the final system where the rock, injected fluid (LSSW10) and crude oil are all present, the changes in the pH are substantially governed by the reactions between both fluids. The initial and intermediate systems are dominated by the existence of formation water. This is not surprising, because the high salinity maintains stable conditions. As soon as the system is dominated by the low salinity water (less amounts of high salinity water), the dependence on the fluids' interaction is greater. It can also be seen from Table 4.4 that the initial and intermediate phases are similar when the pH of the fluid/fluid interaction is above 6. However, when the pH of the aqueous phase is ≤ 6, the final system tends to be modified or altered. Undoubtedly, there is a reorganization of the crude oil compounds, allowing some of them to migrate to the water of low salinity by creating more acidic conditions in the system thus encouraging the dissolution of the rock.

To monitor a possible interchange of ions during this group of tests, samples of the brines were collected and analysed before and after the contacts. The brine composition analyses did not reveal any major changes or modifications in ion concentration of the brines. For instance, the concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} showed a very small variation. The temperature and gently shaking the glasses were not contributing elements for large alterations in the findings.

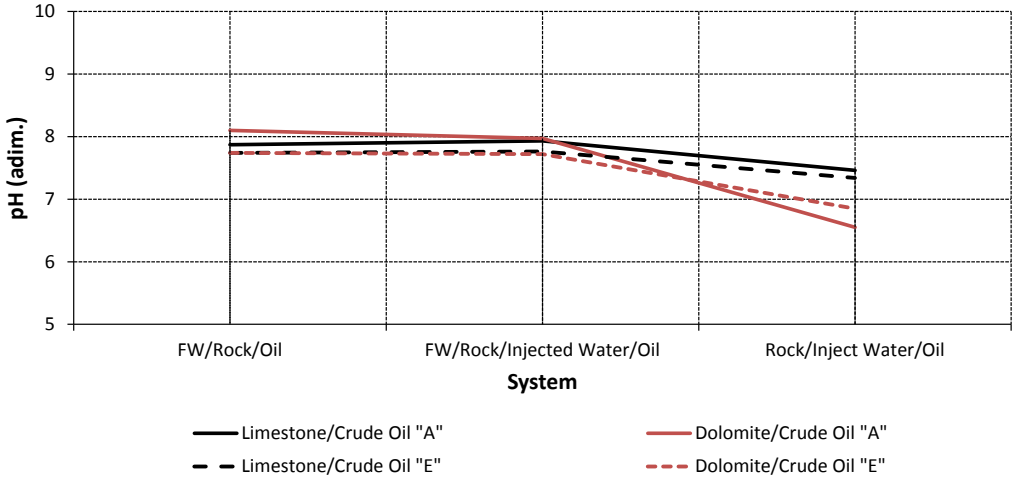

Figure 4.14: pH vs different systems for two carbonate formations.

4.3.1.3 Investigating the Real Impact of the Dissolution Utilising Single Phase Experiments

The effect of the aqueous phase pH and the ion interactions between fluids and rocks was investigated at static conditions. The results indicate that the initial, intermediate and final systems all depend on the interaction of the fluids. It is reasonable to think that the behaviour of the fluids in interacting would be more representative under dynamic conditions. With the flow of fluids, dissolution should be accelerated. In particular, the dissolution that occurs would be faster because other variables would be playing an important role in this mechanism, such as flow rates, transport, pressure and temperature. To define exactly to what extent the mineral dissolution could be accelerated and used as a model system to develop a better understanding of the benefits of low salinity water injection, other experiments should help to explain this phenomenon. If the rock dissolves, the dissolution can be measured in certain ways: 1) from the weight loss of the core, 2) from variation of the permeability or 3) from the concentration changes of ions in the effluents. Although coreflood tests may be helpful in evaluating the permeability reduction under certain conditions, a more detailed knowledge of such changes which could occur within the rock is important. Therefore, an easy way to evaluate the impact of the injection fluids is by measurement of the rock permeability. Experiments were then designed to permit assessment of dissolution using these methods, which allow us to evaluate the dissolution occurs, where it occurs and

how it is influenced by the low salinity waters. Firstly, permeability changes can be studied using Darcy´s Law and these can also be detected by means of ion concentration variations. Therefore, three set of experiments were performed with limestone cores. The objective was to experimentally investigate if mineral dissolution could be detected in a single phase (water) present in the pore spaces. These studies included formation water (FW) because the use of FW ensures that the equilibrium is maintained. This makes this method a good choice for observing any possible changes or interactions between injected fluids and rocks.

In the single phase experiments, all the selected cores were placed in a horizontal position and fully saturated with formation brine (overburden pressure of 500 psi). The cores were previously cleaned with solvents. During the injection of the different brines, the cores were monitored and produced water (effluent) was collected for every pore volume (PV) injected (Figure 4.15). The ion concentration analysis obtained from effluent (IC analysis) and pH of the collected samples were also measured. For the water samples, the electroneutrality was also corroborated, which is a common quality control method. The principle of electroneutrality requires that the sum of the negative ions must equal the sum of negative ions in solution. Finally, pressure differential at specific flow rates was used to calculate the brine permeability. Usually, the permeability decline is calculated by examining the variation of the permeability ratio with respect to the pore volume (Khilar and Fogler, 1984 and Bagci et al., 2000).

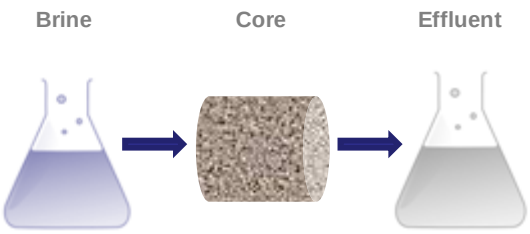

Figure 4.15: Schematic representation of the single phase experiment at room temperature (overburden pressure= 500 psi).

For the first experiment, the sequence of injection was to inject at least 30 pore volumes of FW and the flow rate was held at constant flow rates of 5, 10, 20 and 30 cm^3/hr. After this, LSSW10 was injected at the same flow rates and pore volumes. The experiment finished with the injection of FW. In the second experiment, the low salinity water was substituted by the same low salinity water but which had previously been in contact with crude oil "A", LSSW10CCOA. In the third experiment, the second fluid was replaced with low salinity water which has been in with crude oil "E" (LSSW10CCOE). All flow rates of injections and pore volume injected were respected. For each flow rate, a constant pressure drop was achieved, then the flow rate was switched to another in the same direction.

As mentioned above, the water samples were evaluated. The principle of electroneutrality was used for all water samples and each test was run twice. Variation in duplicate water samples was around ±3 %, which is of greater significance in lower ion concentrations compared to higher concentrations. In general, they presented slight deviations from their original concentrations. Figure 4.16 below illustrates the variations in ion concentrations and pH values for the first test. For magnesium, no major variations in the concentrations occurred. Concentrations of sulphate and calcium rose a little after the injection with LSSW10 and then remained stable at those values. Apart from this, the rest of the ion concentrations did not display any important variations. With regard to pH, the values fluctuated during the first 30 pore volumes injected then rose steadily before being stabilised for the next pore volumes injected (from 50 to 60 pore volumes injected). With the second injection of FW, the values dropped off and reached similar values to those for the first injected volumes.

The system in Test 1 exhibited similar behaviours when two different brines were injected, Table 4.5. At low flow rates, only reduced damage to the rock was observed with FW at 5 cm^3/hr. Note that this possible damage continued to be present as long as the second injected fluid was flowing throughout the core and with a high flow rate but the possible damage was rapidly eliminated when more pore volumes were injected. At high flow rates, the dissolution, if it occurs, is in fast motion avoiding the deposition of particles or salts. ΔP values were very stable during the whole experiment and no

pressure disturbances at different rates were observed. In summary, the permeability decreased imperceptibly when LSSW10 was injected.

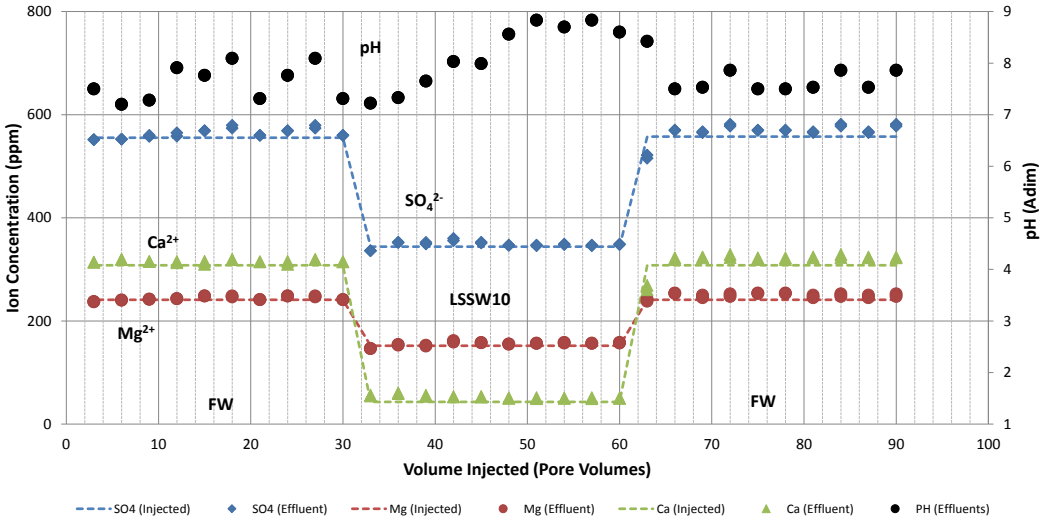

Figure 4.16: Concentration profiles of Ca^{2+}, Mg^{2+} and SO_4^{2-} for the first experiment evaluating the permeability of one core.

Table 4.5: Effect of low and high salinity water injection on the core permeability at certain injection rates for the first core.

Formation Water			**Low Salinity Water**			**Formation Water**		
Rate (cm^3/hr)	**DP (psi)**	**k (md)**	**Rate (cm^3/hr)**	**DP (psi)**	**k (md)**	**Rate (cm^3/hr)**	**DP (psi)**	**k (md)**
5	1.72	36.83	5	1.50	39.72	5	1.93	32.82
10	2.95	42.95	10	2.92	40.82	10	3.5	36.20
20	6.02	42.05	20	5.85	40.74	20	7.30	34.71
30	8.90	42.70	30	9.30	38.44	30	10.90	34.87
Average		**41.13**	**Average**		**39.93**	**Average**		**34.65**

The second test was performed with a limestone core with pore volume 15.21 cm^3, length around 15.2 inches and diameter 2.51 inches. The analysis of the effluents when the core was flowed through with formation water revealed that the concentration of magnesium, sodium and sulphate remained unchanged. Ion movement was observed only when the fluid was changed. Ion concentrations varied from 31 to 60 PV. The sulphate and calcium were very active, being released from rock surface when low salinity water treated with crude oil "A" was injected (Figure 4.17). The production of sulphate continued during new injections of FW. On the other hand, calcium fell slightly for this last step.

The changes of injected brines and flow rates resulted in rises in pH values, with variations composed of irregular increases and decreases. Again, the same behaviour as in the first experiment was exhibited during injection of FW, for the first step. A different trend was observed when the permeability was evaluated with the second brine at 5 cm^3/hr. After the low salinity water flowing through the core was switched from FW to LSSW, it can be observed from Table 4.6 that the brine permeability of the core dropped dramatically, by a factor of about 70, after only 2.5 pore volumes of LSSWCCOA had entered to the system. The value changed but recovered at high injection rates (10, 20, and 30 cm^3/hr) with this second fluid, as shown in Table 4.6. The permeability decreased with the subsequent flow rates, presumably because the low salinity water was working as acidic water (pH~3.70). Additionally, the differential pressure measurements were unstable, giving divergent permeability values. The permeability for this second brine finally fell by up to 36.26 % from the original value of 19.47 md.

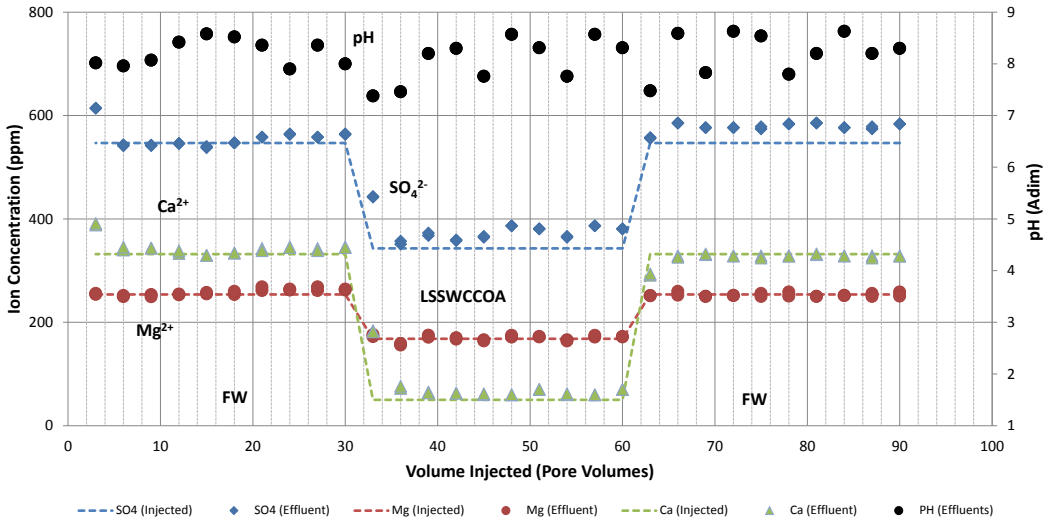

Figure 4.17: Concentration profiles of Ca^{2+}, Mg^{2+} and SO_4^{2-} for the second experiment evaluating the permeability of one core.

A partial recovery of the permeability value is noted with the injection of FW as a third fluid. It is possible that this change of injected water could have removed the possible plugging of the pores by precipitations. For this final FW injection, the permeability recovery was permanent and the differential pressure (ΔP) was once more stable. At high flow rates, the damage was practically removed and the injected water was able to displace the liberated material from the rock. The final value of the permeability was around 10.32 % less, which was not considered significant. The initial permeability was practically recovered.

The extent of permeability reduction would depend on the margin by which the flow rate has declined, being more critical for low salinity fluids when they are in contact with crude oils with high TBN. Low salinity injection is mobilizing detached material from the cores at high rates and may be causing damage via pore throat obstruction at low rates. This type of water (low pH) is incompatible with the cores. The effect of the generated acidic water can be detected in the differential pressure and the permeability reduction factor. Figure 4.18 illustrates the experimental data for one flow rate used (30 cm^3/hr); k/k_o and ΔP are plotted as a function of pore volumes for the second and third brines, where "k" is the permeability at a particular time, and "k_o" is the initial

permeability. A significant difference occurs in ΔP between both fluids. With FW brine, the variation was shown to be minimal but with LSSWCCOA fluid, it was evidently impossible to maintain stable behaviour and the action of this water caused a variation in the permeability.

Table 4.6: Effect of low and high salinity water injection on the core permeability at certain injection rates for the second core.

Formation Water			**Low Salinity Water Treated with Crude Oil "A"**			**Formation Water**		
Rate (cm^3/hr)	**DP (psi)**	**k (md)**	**Rate (cm^3/hr)**	**DP (psi)**	**k (md)**	**Rate (cm^3/hr)**	**DP (psi)**	**k (md)**
5	3.52	17.91	5	9.43	6.09	5	4.16	15.15
10	6.30	20.02	10	9.95	11.54	10	6.70	18.82
20	12.80	19.70	20	16.96	13.54	20	14.00	18.01
30	18.65	20.28	30	18.70	18.47	30	21.17	17.87
Average		**19.47**	**Average**		**12.41**	**Average**		**17.46**

Near the final stage of the injection at this rate, the permeability reduction factor is close to the unit (k/k_o= 1). However, it is clear that at some point the permeability value can increase if injection at this rate continues. It is worth noting that high flow rates could generate channels due to the constant injection in one direction, avoiding piston-like displacement.

For the third experiment, ion concentrations remained stable and without changes for the first 30 pore volumes injected, as shown in Figure 4.19. With the second injected water, LSSWCCOE (pH= 6.36), there were no noticeable changes. For the situation where formation water was again injected into the core, the concentrations of the main ions did not suffer significant variations; however, the analyses revealed a small variation of concentration of calcium and sulphate. This variation may be related to a reaction between the rock and the second injected brine, which could have caused increased concentrations of these ions.

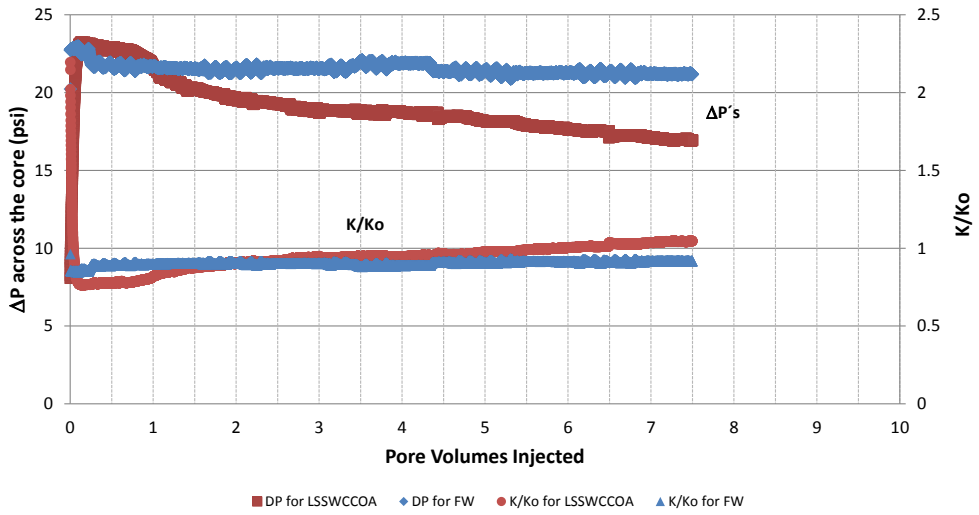

Figure 4.18: Permeability and pressure response for two different brines.

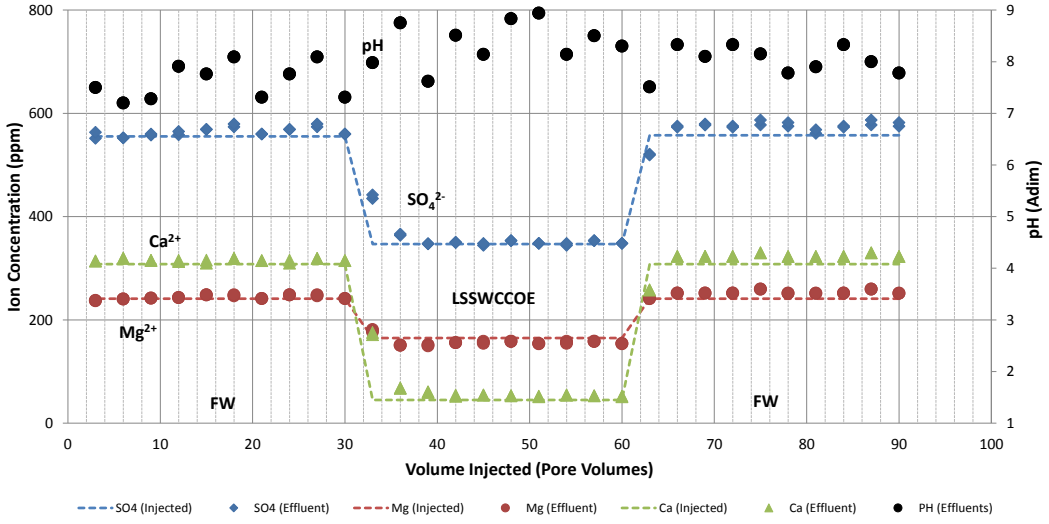

Figure 4.19: Concentration profiles of Ca^{2+}, Mg^{2+} and SO_4^{2-} for the third experiment evaluating the permeability of one core.

When low salinity water (LSSWCCOE) was injected, changes of permeability were almost imperceptible. Permeability reduction was less severe than with low salinity water treated with crude oil "A". The average permeability of the core before injection of LSSWCCOE was 34.65 md (Table 4.7) and the permeability after injection of 30 pore volumes of LSSWCCOE was 31.20 md. There was approximately 10 % loss in

permeability because of injection of this type of water. When the FW was added, no permeability changes occurred.

Table 4.7: Effect of low and high salinity water injection on the core permeability at certain injection rates for the third core.

Formation Water			**Low Salinity Water Treated with Crude Oil "E"**			**Formation Water**		
Rate (cm^3/hr)	**DP (psi)**	**k (md)**	**Rate (cm^3/hr)**	**DP (psi)**	**k (md)**	**Rate (cm^3/hr)**	**DP (psi)**	**k (md)**
5	1.93	32.82	5	1.88	30.69	5	2.05	30.90
10	3.50	36.20	10	3.60	32.06	10	4.0	31.67
20	7.30	34.71	20	7.50	30.77	20	8.17	31.01
30	10.90	34.87	30	11.07	31.27	30	12.30	30.90
Average		**34.65**	**Average**		**31.20**	**Average**		**31.19**

Even though, it was not possible to detect bicarbonate concentrations using ion chromatography analysis, the effluent samples were treated with methyl orange and then titrated with hydrochloric acid. The most likely source of the discrepancy in the results is in the values of bicarbonates obtained for the LSSWCCOA brine. In Figure 4.20, the results of bicarbonate changes for all experiments are shown as a function of the pore volume. The measurements in Figure 4.20 indicate constant variation for two brines (LSSW10 and LSSWCCOE). This implies that the possible dissolution in both brines is product of the flow rates. Thus, low salinity water mobilises the material released from the rock. At low rates (5 cm^3/hr), the precipitation is probably higher than dissolution, causing formation damage via permeability reduction. At high rates, the injected water is able to remove that damage, if it occurs, and mobilises the salts. The resulting permeability reduction is thus marginal in comparison to that obtained due to the same injected fluid when its pH is reduced to 3.70 (LSSWCCOA). For this last case, the rate of dissolution is faster because the lower pH causes a greater reaction with the rock surface, and the saturation or suspension of the liberated material is also immediate, except for at low flow rates, where the brine is not able to dissolve and transport these additional concentrations. PHREEQC simulations could not adequately predict such behaviours; moreover, this geochemical software overestimated the bicarbonate and

calcium concentrations for the LSSWCCOA and underestimated the production of bicarbonate and calcium for the other waters.

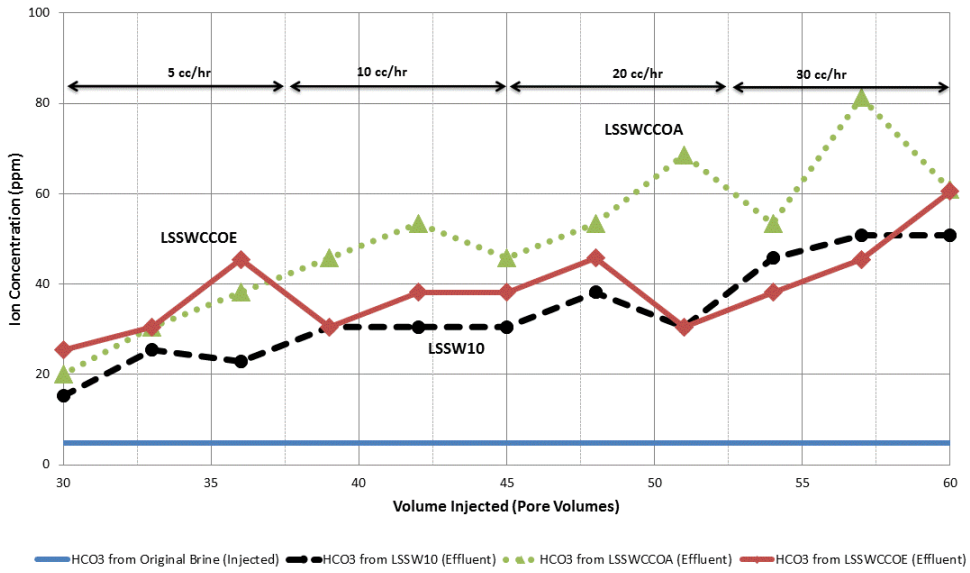

Figure 4.20: Concentration profiles of bicarbonates for the three experiments.

4.4 SUMMARY AND CONCLUSIONS

At this point, four important parameters have been analysed, formation water, type of rock, crude oils and injected waters. Additionally, their effects were evaluated, including pH variations (as a result of the contact with a specific crude oil), changes of the ion concentrations in the effluents and changes in the flow rate. Although this study was limited to single types of low salinity waters in contact with different crude oils, it has been established that the dissolution of the rock is undoubtedly triggered by contact with certain crude oils. These results mean that the chemical interaction between injected water and rock surface occurs in the form of mineral dissolution. The waters for injection can: a) be capable of interacting with the crude oil in order to generate acidic water, b) be unsaturated, allowing the maximum amount of solute to be dissolved, b) be mobile enough to carry the dissolved material outside the rock and c) reduce the chance of developing damage or plugging of the pores. In this investigation of dissolution, it has been found that basic crude oils were the most influential of the crude oils. It is likely that dissolution occurs as a direct and strong result of the flow of the injected water in contact with the crude oil, which generates this mechanism. However, its

presence under static conditions has only a minor impact, because the dissolution rate is likely to be slower.

Therefore, these tests give more realistic assessments of the previously omitted effects of interactions between the fluids, crude oils and injected waters, and subsequently between fluids and rock. Moreover, these studies have helped to explain why, when formation brine only is flowing throughout the cores, although the equilibrium is maintained and the original conditions of the rock remain almost the same, certain amounts of material from the rocks are released, generating an elevated pH. Eventually, this also happens with more aggressive injected waters, where the released material will contribute to increase the pH values. The amount of rock dissolution from carbonate formations detected under static conditions seems to be less compared to that in dynamic conditions, where flow rate is playing an important role. This description of the dissolution phenomenon from consideration of single phase tests and fluid/rock interactions may be very simplistic. Nevertheless, it is a first step to realising the significance of rock-water interaction. The permeability measurements elucidate the importance of the evaluation of the rock permeability before and after each experiment and they usually need to be measured independently under a single phase with compatible or inert fluids, if the target is the dissolution. The results presented here, corroborate this notion.

Since it has been established experimentally that the variation of the brine composition and its previous contact with the crude oil can affect the original permeability value, the next step will be to examine if the same consequences may be ascertained when other variables are involved, such as pressure, aging of the cores and flow rates.

The next chapter will aid us to understand how these basic analyses can be linked to the effects of chemical reactions and interactions between the solute and the rock. Chapter 5 will then try to examine those links between rock and fluids in the course of more complex tests and hence evaluate the enhanced oil recovery either through spontaneous imbibition or coreflood experiments.

CHAPTER 5 – MAIN RESULTS AND DISCUSSION

INTRODUCTION

Since it has been analytically established that the interactions of crude oil/smart water (especially low salinity waters) can naturally generate acidic water during water injection in carbonate rocks, the goal of this chapter will be the validation of these observations. The lack of equilibrium in the fluid/rock system may be the underlying cause of changes in wettability and rock dissolution due to such chemical interactions between invading fluids and the initial native fluids, principally with the crude oils. For this reason, one cannot confirm these facts without considering the flow of fluids throughout the cores at reservoir conditions. Moreover, the possibility that these conditions would involve the pressure and its influence cannot be excluded either. Considering that dissolution has been identified as part of the effects that occur during smart water injection, especially in low salinity waters, coreflood experiments should enable us to observe the difference in the enhanced oil recovery if different brines and crude oils are used. This will make it possible to distinguish where and when this vital mechanism occurs.

As indicated in Chapter 4 of this work, there is probably a pattern that proves that dissolution plays an important role during the additional oil production. Therefore, this chapter will mainly focus on more elaborate experiments such as spontaneous and coreflood experiments where it will be demonstrated how the simple models previously presented can be used to predict if dissolution of the rock is taking place in the fluid/rock interaction and then to evaluate its impact on final oil production. Firstly, a short description of the variables that affect rock dissolution will be given. Part of this chapter is devoted to identifying the contact angle values for two specific crude oils under several aqueous phases and rocks. These values are used to predict the nature of the wettability status; however, in the context of pore-scale dynamic conditions they do not offer a way to observe the dynamic processes of the interactions. Nevertheless, they allow us to know whether the wettability change occurs and how this change of initial condition is influenced by different types of aqueous solutions. Subsequently,

spontaneous imbibition (SI) tests were performed, using both limestone and dolomite cores with a group of brines and a basic crude oil. Coreflood experiments were then carried out under both secondary and tertiary injection modes, in order to experimentally investigate the performance of smart water injection for heavy oils. The effects of the composition of the crude oil on the dissolution of rock were also studied and compared in terms of additional oil recovery. Water composition changes, pH measurements, permeability variations and oil recoveries before and after the experiments were all performed during the experiments. That will allow us to examine the fundamentals of fluid flow and analyse whether changes occur, where they occur and how they are influenced by the injected waters. The chapter ends with the discussion of what implications these results will have for the oil production of carbonate heavy oil reservoirs. The results of this chapter will supplement previous findings.

5.1 DISSOLUTION OF CARBONATE ROCKS

As was seen in Chapter 2, Carbonate rocks generally consist of 3 types of rock: limestone, which is the most common, dolostone, or dolomite, and chalk, which is constituted by the highest amount of calcium carbonate. They easily react to acidic water, creating rock dissolution, but this may precipitate in alkaline solutions. Of course, dissolution is also affected by other variables, such as pressure, temperature, rate controlling mechanisms, type of aqueous phase, pH and ionic strength, and CO_2 content or the presence of inhibitors.

Dissolution of the rock is usually studied in the context of room conditions and hence research for elevated temperatures or pressures is limited in the published literature (Morey, 1962; Plummer at al., 1978, Zhang et al., 2007). For instance, calcite and dolomite minerals have been investigated in terms of the importance of transport control vs pH changes. In calcite analysis, it was found that, for pH < 3.5, the extent of dissolution is controlled by transport, while for the higher pH zone, it is more dependent on the solution chemistry, Figure 5.1 (Brantley, 2008). Sjoberg and Rickard (1976, 1978, 1983, 1984 and 1985) undertook much work on temperature and pH dependency. Figure 5.2 depicts three important regions. In region 1, where the dissolution is faster, a

H^+ dependent section is dominated by mass action. For region 2, they explain that in this zone the calcium concentrations did influence the pH. Once the calcium increases, the pH also increases and the reaction mechanisms for region 3 may vary from those in the previous zone until equilibrium is achieved. Temperature was also studied. When the temperature goes up diffusion will control the system. At low temperatures, dissolution is a chemical control mechanism.

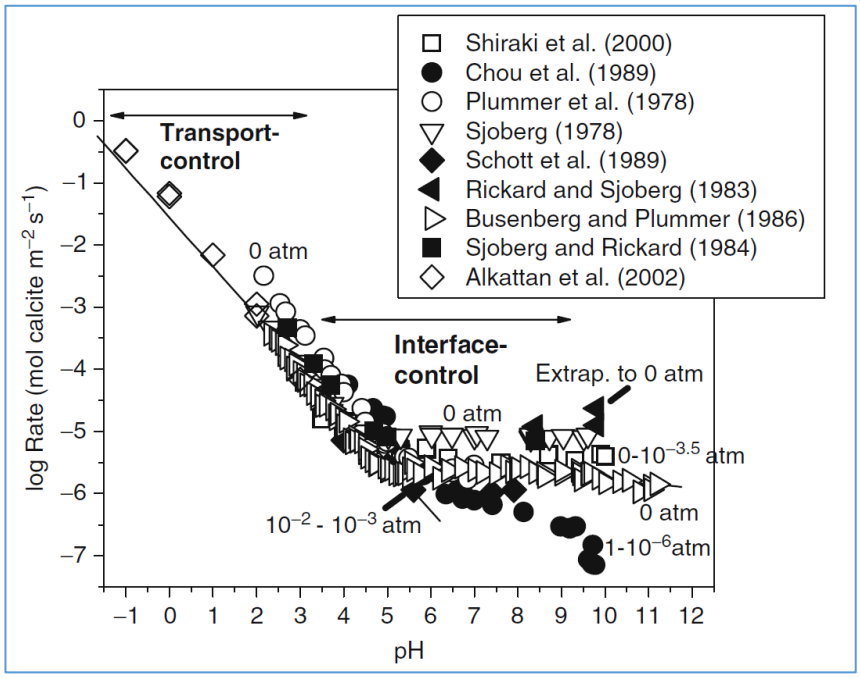

Figure 5.1: Diagram of calcite dissolution as a function of pH and dissolution rates (Modified from Brantley, 2008).

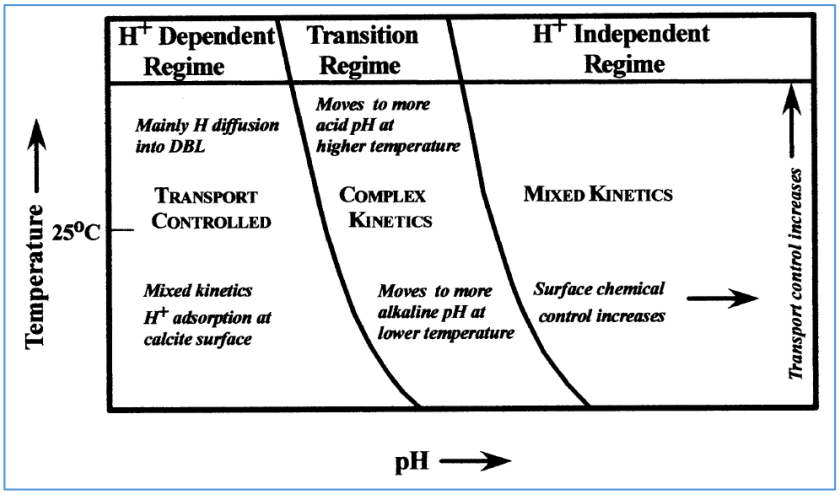

Figure 5.2: Scheme of rate controlling mechanisms for calcite dissolution (Modified from Morse and Arvidson, 2002).

Morse and Arvidson (2002), Figure 5.3, compiled dolomite dissolution data as a function of pH, from published values. Below pH 4, the dolomite dissolution is also dependent on the transport. It is evident that the dissolution rate for the calcite mineral is faster than for the dolomite. The experiments of Zhang et al. (2007) indicate that the mechanisms of dissolution of dolomite at low temperatures differ from those at high temperatures. Their results indicate that there are linear correlations between concentrations of calcium and magnesium in the aqueous phases. The release rates of calcium and magnesium are proportional (1:1), especially at temperatures below 100^{o} C. However, the dissolution product is incongruent at higher temperatures. The concentration of dissolved calcium did not show a linear correlation with magnesium concentration in the effluents. Their observations were in line with Morey's work in the early 60's. In his work with dolomite ($CACO_3 \cdot MgCO_3$), the concentration of $CaCO_3$ increased up to 200^{o} C, then suffered a dramatic fall. $MgCO_3$ concentration increased in CO_2-free water up to 100^{o} C then also dropped. Both observations were congruent up to as high as 80^{o} C (1:1 dissolution) but above that the solution was non-stoichiometric (unequal proportions for a specific chemical reaction).

Caciagli and Manning (2003) conducted a study to determine the effect of high pressure and high temperature on the solubility of calcite in water. According to these authors, pressure has a strong effect on calcite solubility. Similar results were also obtained by Coto et al. (2012), in the presence of CO_2. The calcium carbonate solubility seemed to increase at higher partial pressure of this gas.

In addition, a rise in the dissolved concentration of calcium or magnesium in the aqueous solutions usually decreases the dissolution rate for the calcite. In this case, the named ions may act as inhibitors. The function of the inhibitors for calcite was exhaustively reviewed in Morse and Arvidson's work (2002). Strontium, barium, transition and heavy metals, sulphate, phosphate, silica, nitrite and organics were listed and mentioned as important for the dissolution rates. The combined influences of the calcium and magnesium showed that they have a greater effect on calcite dissolution than other ions. On the other hand, Zhang and al. (2007) found that dissolved calcium is a strong inhibitor for dolomite dissolution, in most cases. Magnesium was found to be less active as an inhibitor at low temperatures but at high temperatures (from 100 to

250^{o} C), dissolution rates of dolomite were increased with increasing in the concentration of dissolved magnesium.

Thus, a vast number of studies have provided evidence that the rate of dissolution is highly dependent on diverse variables. Under reservoir conditions where such variables are important, smart waters may then apparently mobilise the released material from the core and produce/transport it to the outside. The observation that smart waters may mobilise this material also suggests that movement and transport are likely to occur during coreflood experiments, in either secondary or tertiary oil recovery methods at high pressure and high temperature, even at reservoir scale, where reservoir conditions could favour better situations for dissolution and transport. Thus, complex experiments could verify many of the concepts described earlier.

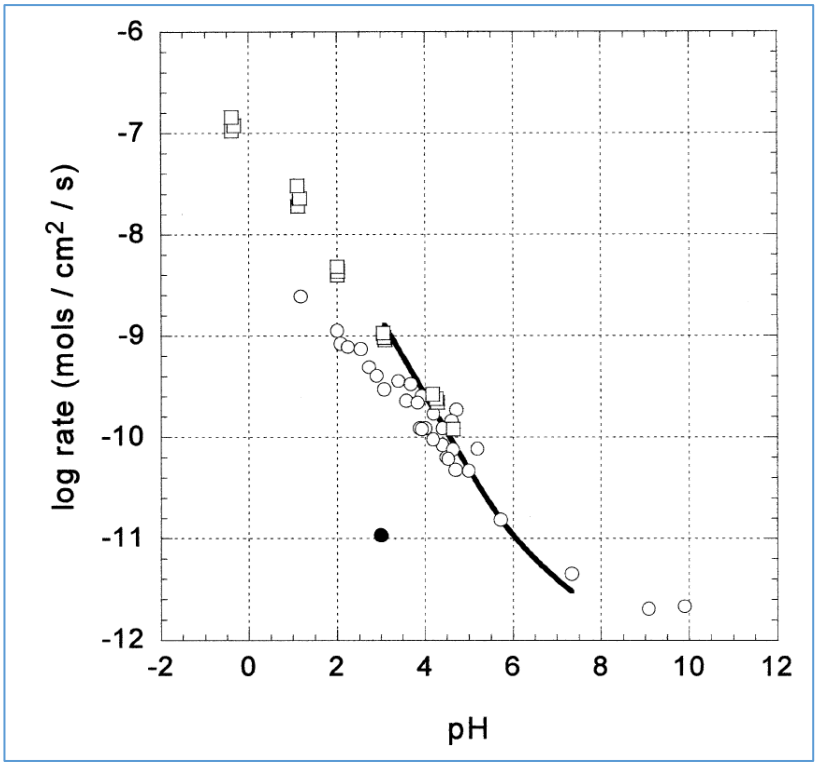

Figure 5.3: The dissolution rate of dolomite as a function of pH (Modified from Morse and Arvidson, 2002).

5.2 CONTACT ANGLE MEASUREMENTS AND ADHESION TESTS

Many studies have shown that composition and mineralogy can have a great impact on wettability (Buckley, 1996). Carbonate surfaces normally have positive charge with pH less than 9, which aids the attachment of negative acidic compounds from the crude oils to the rock surfaces offering oil-wet conditions. A large number of studies on the relationship between oil composition and wettability have been conducted by Buckley and co-workers (1989, 1992, 1995-1998). Moreover, Chilingar and Yen in their extensive work found (1983) that, principally, carbonate reservoirs are more oil-wet than intermediate wet systems. Previously Treiber et al., in 1972, had already come to the same conclusions. They observed that around 84 % of the carbonate reservoirs tested were oil-wet and 8 % were intermediate-wet systems. Nevertheless, experimental results on wettability alteration in heavy oils are rare. This subsection attempts to describe the wettability within the rock slabs as a function of two crude oils.

Contact angle measurements were conducted on both limestone and dolomite plates with two crude oils. To avoid oil drop imbibition and rough surfaces, the plates or slabs (25 x 25 x 4 mm) were polished and cleaned with solvents. Special care was taken with the selection of the contact areas between the crude oil and the rock surface in order to establish a correct evaluation of this parameter. The slabs were first immersed in the formation water for equilibrium, and then they were left at an elevated temperature, as described in Chapter 3. After the equilibrium, some thin sections were aged with the crude oils at an elevated temperature for the same period of time, and then the excess crude oil was removed from the surfaces and put in contact with the working brine. Other slabs were directly taken and the extra formation water was also removed and once again put in contact with the selected brine before starting the experiment. Figure 5.4 shows the crude oil drop in contact with a limestone plate placed in the holder. All these experiments were conducted at room temperature. Most of the experiments were repeated; the results were similar but not identical. This may be attributed to different levels of surface irregularity or be dependent on the presence or absence of certain minerals, as has been reported in the published literature (Hirasaki, 1991 and Buckley et al., 1989).

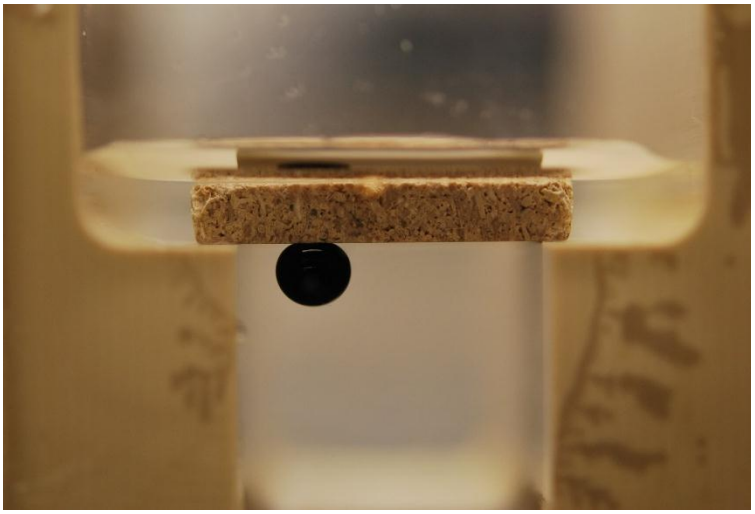

Figure 5.4- Crude oil drop in contact with the rock surface in a special holder.

Figure 5.5 depicts wettability measurements obtained with different types of rocks, using first formation water, then crude oil and then either seawater or low salinity seawater. Both rocks exhibited a significant change in the contact angle for low salinity seawater diluted ten times with the crude oil "A", which indicated that the rock wettability is a water-wet system. In the seawater case for the limestone rock, the contact angle indicated an intermediate wettability state (Anderson, 1986). With slabs aged with an acidic crude oil, the results changed, giving more oil-wet conditions for the dolomite plates.

It is seen that the adsorbed amount was higher for the acid-rich crude oil (TAN>0.5 mg KOH/g) than for the base-rich crude oil (TAN<). This is in line with previous results, where the positive surface of the rock rules out being prone to having oil-wet systems. It has been thus verified that the oil wetting nature of carbonate surfaces seemed to increase as the Total Acid Number (TAN) increased (Standnes and Austad, 2000; Standnes and Austad, 2003; Zhang and Austad, 2005).

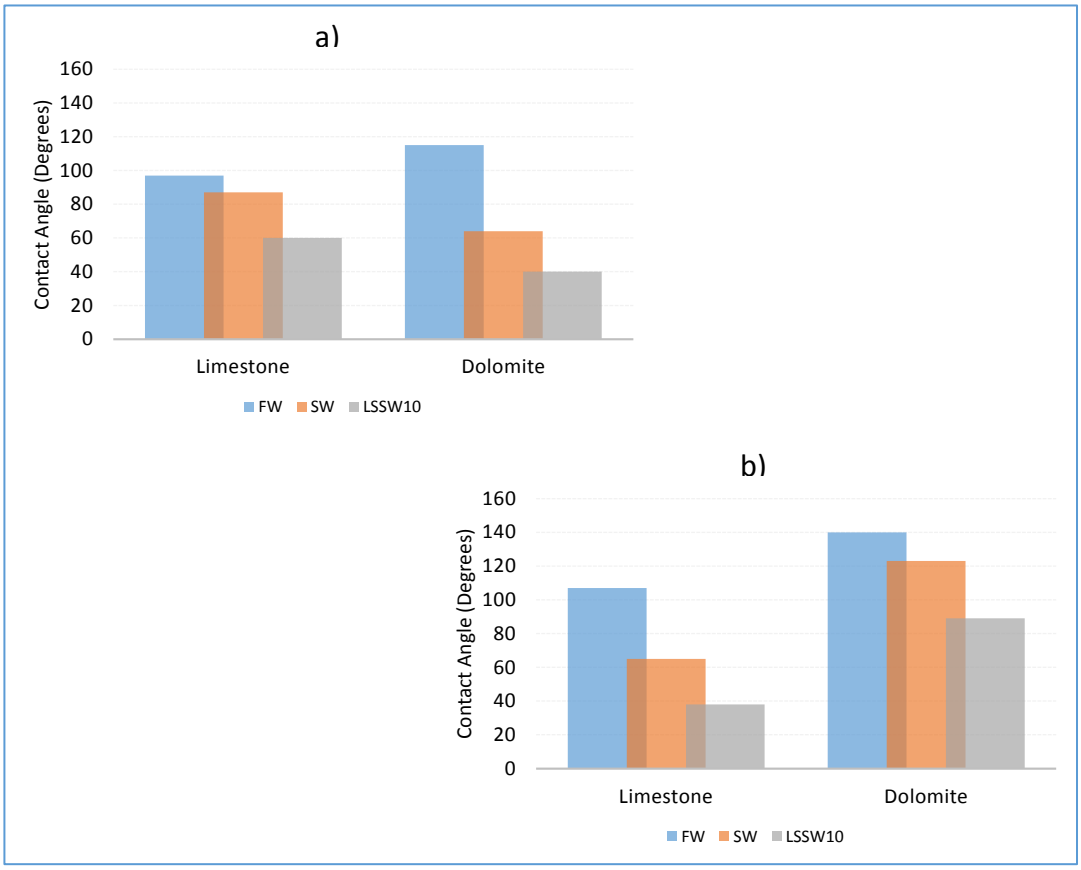

Figure 5.5: Wettability alterations by both crude oils: a) crude oil "A" and b) crude oil "E".

Therefore, the efficacy of water injection should be higher for crude oil "A", which alters the wettability of the rock to be less oil-wet. If a surface is first in contact with formation brine, a low contact angle can result when it is then in contact with different brines (Figure 5.6). These results indicate that if the surface is only in contact with water, the contact angle will be $<90^{o}$. The contact angle in the aqueous phases could describe the ideal state of the rock after an efficient waterflood process.

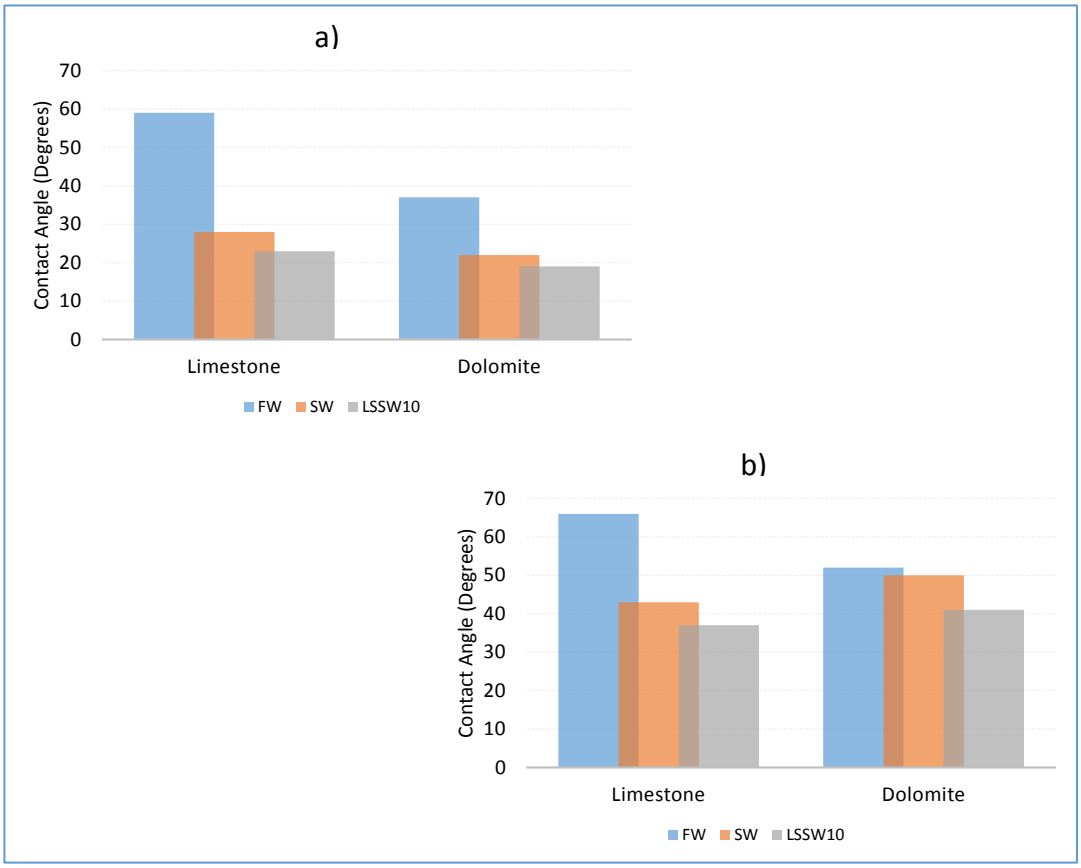

Figure 5.6: Wettability alterations by both crude oils when the slabs are only exposed to brines: a) crude oil "A" and b) crude oil "E".

A simple and modified method, using measurements of adhesion tests, was utilised to quantify whether the crude oil could show attraction towards the carbonate surfaces (see Chapter 2 for a description of this method). The results of a very short exposure of the area to a crude oil drop are shown in Table 5.1, in terms of adhesion or non-adhesion.

Table 5.1: Simple adhesion tests for two crude oils.

Rock	Rock/FW/ Crude Oil/SW	Rock/FW/ Crude Oil/LSSW10	Rock/FW/SW	Rock/FW/ LSSW10
	Crude Oil "A"			
Limestone	Adhesion	Adhesion	Non-adhesion	Non-adhesion
Dolomite	Adhesion	Adhesion	Non-adhesion	Non-adhesion
	Crude Oil "E"			
Limestone	Adhesion	Adhesion	Non-adhesion	Non-adhesion
Dolomite	Adhesion	Adhesion	Non-adhesion	Non-adhesion

The slabs previously aged with crude oil almost always fell into the adhesion type. In general, crude oil "A" turned out to be less disposed to be attached to the plate surfaces. The adsorption of this crude oil seems to be governed by the lack of the oil-soluble compounds which dictate the state of wettability. Although its asphaltene and resin content is higher, the attraction to the rock surfaces was less significant than the most acidic crude oil. Conversely, the crude oil "E" was identified as a crude oil capable of having strong adhesion to the rock surface.

The non-adhesion observed in these analyses is likely to be due to the rapid action of the water. Extra time and additional pressure were needed so that the crude oil drops could adhere to the rock surface, see Figure 5.7 below. This largely occurs when the surface become more hydrated, generating a stronger water film. This is explained in view of different hydration energies at the mineral surfaces (Pokrovsky et al., 2000). For limestone surfaces, the calcium cation is the major contributor to binding water molecules. For dolomite surfaces, the degree of hydration depends on the magnesium and calcium cations. The former have a much higher affinity towards water molecules; consequently, the water film will be stronger. Moreover, the crude oils may be negatively charged at high pH (Healy and al., 1978; Buckley and al., 1989, Dubey and Doe, 1993 and Jada and Salou, 2002).

This implies that the crude oil "A" was negatively charged in contact with the brines but the dominant positive charges prevent the attraction due to the positive surface of the rock and a stronger water film, and thus the repulsion forces between the rock and the crude oil are dominating the system. This is particularly noticeable for the dolomite slabs which were more water-wet, see Figure 5.6a. In addition, the crude oil "E" was more negatively charged, causing a better adhesion to the rock surfaces; hence the systems were less water-wet. It is clear from the work here that crude oil "E" tended to strongly adhere to the surface of the plates. The adsorption was also stronger when a wetting-water film existed, which became less relevant with the presence of this crude oil, especially for the dolomite case. RezaeiDoust et al. (2009) summarise certain conditions that help to change the wettability conditions to more water-wet.

They affirmed that these involved high temperatures, > 90^{o} C, and divalent ions contained in the injected water, which would be more active and help to improve such changes in wettability. These assertions could not be confirmed and will be discussed in detail later on.

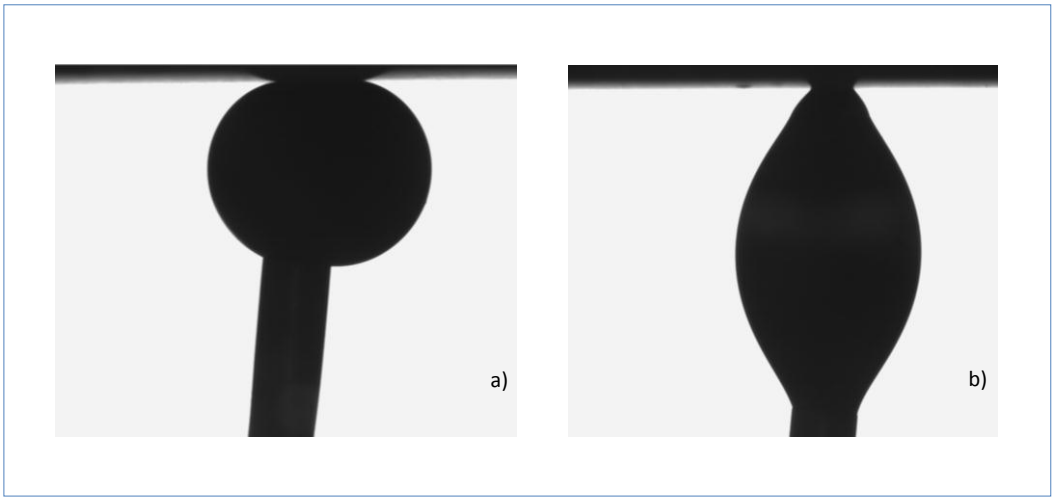

Figure 5.7: Adhesion tests for the crude oil "A" (slabs were not aged with the crude oil), a) excess of pressure necessary to allow the attachment of the crude oil drop and b) the crude oil drop is easily withdrawn from the rock surface.

To extend the previous investigations, brine samples were collected and evaluated for their concentration and pH after the contact angle measurements. The brine composition analysis did not reveal any major changes or modifications in ion concentrations of the brines. It was important to have an accuracy of ± 3.0 % in the results because the analysed volumes were very small. The pHs were measured and showed small variations from their original values, as shown in Table 5.2 below. Plates aged with crude oil represent system "c", described in Figure 4.13 and Table 4.4, and system "d" represents the final part of the injection. In general, the pH values tended to increase slightly. Even if the pH of the water samples has changed, the dissolution, if it exists, will be time-dependent. Additionally, the volume of oil (≈30 μl) was not able to create an acidic state for the systems with only brines, because it is practically negligible. It is conceivable that the presence of a system with a very small volume of crude oil cannot really affect the established system. This may reveal that the movement of the fluids and the volume of crude oil present could accelerate the interaction between the injected brine and the water-soluble compounds, leading to higher and faster rock dissolution,

and an improvement in the wettability state. According to this analysis, crude oils and injected waters will become more active, as there will be a flow of fluids.

Table 5.2: Behaviour of the pH for estimations of the presence of dissolution at static conditions for low salinity water.

	(a)*	Contact Angle	(c)*	Contact Angle	(d)*	Contact Angle
Systems with Crude Oil "A"			**Limestone**			
Brine	8.01	8.01	7.75	7.75	7.20	7.20
Brine (s)/Rock	8.39	8.47**	7.99	-	8.16	8.10**
Brine (s)/Rock/Crude Oil	7.93	-	7.87	7.81**	7.46	-
Brine(s)/Crude Oil*	8.02	-	8.01	-	3.70	-
			Dolomite			
Brine	8.01	8.01	7.75	7.75	7.20	7.20
Brine (s)/Rock	8.50	8.55**	8.05	-	7.50	7.42**
Brine (s)/Rock/Crude Oil	8.10	-	7.97	7.92**	6.55	-
Brine(s)/Crude Oil*	8.02	-	8.01		3.70	-
Systems with Crude Oil "E"			**Limestone**			
Brine	8.01	8.01	7.75	7.75	7.20	7.20
Brine (s)/Rock	8.39	8.43**	7.99	-	8.16	8.09**
Brine (s)/Rock/Crude Oil	7.76	-	7.74	7.76**	7.34	-
Brine(s)/Crude Oil*	7.98	-	7.85	-	6.36	-
			Dolomite			
Brine	8.01	8.01	7.75	7.75	7.20	7.20
Brine (s)/Rock	8.50	8.57**	8.05	-	7.96	7.70**
Brine (s)/Rock/Crude Oil	7.74	-	7.72	7.73**	6.85	-
Brine(s)/Crude Oil*	7.98	-	7.85	-	6.36	-
System						

*Previously analysed, chapter 4. **Assuming that one crude oil drop was in contact with this system.

The results indicate that under static conditions the low salinity injection may alter the natural state of wettability to be more water-wet for the basic crude oil. Low salinity water may be effective for dolomite rocks when it is used for this type of crude oil. On the other hand, neither seawater nor low salinity water can promote major changes in the wettability status for dolomite cores in contact with acidic crude oils. The wettability of these types of reservoirs could then vary microscopically or macroscopically. The contact angle measurements and adhesion tests offered a quick,

simple and semi-quantitative means for characterizing crude oils with respect to their interactions with brine and plates.

5.3 SPONTANEOUS IMBIBITION TESTS

In this part of the chapter, seven carbonate cores were selected to study how smart waters may affect imbibition rate at the same temperature. As described in subsection 3.3.3, carbonate cores were placed in glass cells at high temperature to imbibe crude oil "A" from the cores. Cores Lim-4, Lim-5, Lim-6, Lim-7, Dolom-1, Dolom-2 and Dolom-3 were tested in these experiments. Seawater and low salinity seawater (LSSW10) were used as imbibing fluids. The results are shown in Figures 5.8 and 5.9. In static experimental conditions, viscous forces are negligible in comparison to gravity and capillary forces. Both of these forces are discussed in this subsection, since these are the forces that control the static imbibition processes.

Ma et al. (1997) proposed a semi-empirical scaling group to correlate spontaneous imbibition behaviour for strongly water-wet systems. They modified the original equation developed by Mattax and Kyte (1962) changing the dimensionless scaling parameters and included the concepts of characteristic length and the effect of water and oil viscosities. So, the original equation was then redefined as follows:

$$t_D = 0.018849\mathrm{t}\sqrt{\frac{k}{\phi}}\frac{\sigma}{\sqrt{\mu_o \mu_w}}\frac{1}{L_c^2} \qquad 5.1$$

Where t_D is the dimensionless time, t is the current time of imbibition, and ϕ and k are the porosity and permeability of the core sample, respectively, σ is the interfacial tension, μ_w and μ_o are the water and oil viscosities and L_c is the characteristic length. This last variable is the length that balances the effect of boundary conditions, type of shape and size of the core sample. For all open faces, L_c is defined as:

$$L_c = \frac{Ld}{2\sqrt{d^2+2L^2}} \qquad 5.2$$

where d and L are the diameter and length of the core sample, respectively. Use of this scaling group to compare the spontaneous imbibition results of cores with wettability states other than strongly water-wet systems has offered a satisfactory scaling method for weakly water-wet and mixed-wet situations (Xie et al., 2000 and Tong et al., 2001). Scaled spontaneous imbibition results for the chosen carbonate cores are presented in Figures 5.8c and 5.9c.

Limestone cores surrounded by seawater brines showed rises in oil recovery of up to 16.5 %. In general, the results from each of these cores indicated roughly the same oil recovery when seawater was used. The test on the core with the lowest permeability was stopped due to unexpected problems. At early times (Figure 5.8a), it can be seen that imbibition is dominated by capillary forces and then crude oil is expelled from all the faces of the cores, except for Lim-6 where gravity forces were expected to control the rate of imbibition. Later, as the rate of imbibition reduces, gravity forces become more important for the oil production. This situation is illustrated in Figure 5.8b. After 30 days, the oil recovery has almost reached its maximum value and the slope of the rate of imbibition becomes linear. This final change in the curves points to the fact that the gravity forces are dominating the imbibition of crude oil. The oil recovery was primarily dependent on the type of imbibing fluid and the process of imbibition took more time than expected. However, the scaled results, shown in Figure 5.8c, indicate that the rate of imbibition slowed in the cores contacted with seawater as the imbibing fluid. The imbibition data for the different limestone cores reported in dimensionless time coincide, indicating a similar wettability. At different permeability values, there was no substantial increase in total oil recovered. The results for all limestone cores in contact with seawater exhibited quite similar behaviour. These outcomes do not indicate a dependence on permeability. Therefore, it can be stated that the core samples exhibited better conditions of oil-wet systems. On the other hand, low salinity brine was imbibed quickly into the core Lim-7 and around 20 % of OOIP was produced in the first two days. Evidently, there was a change in the wettability conditions.

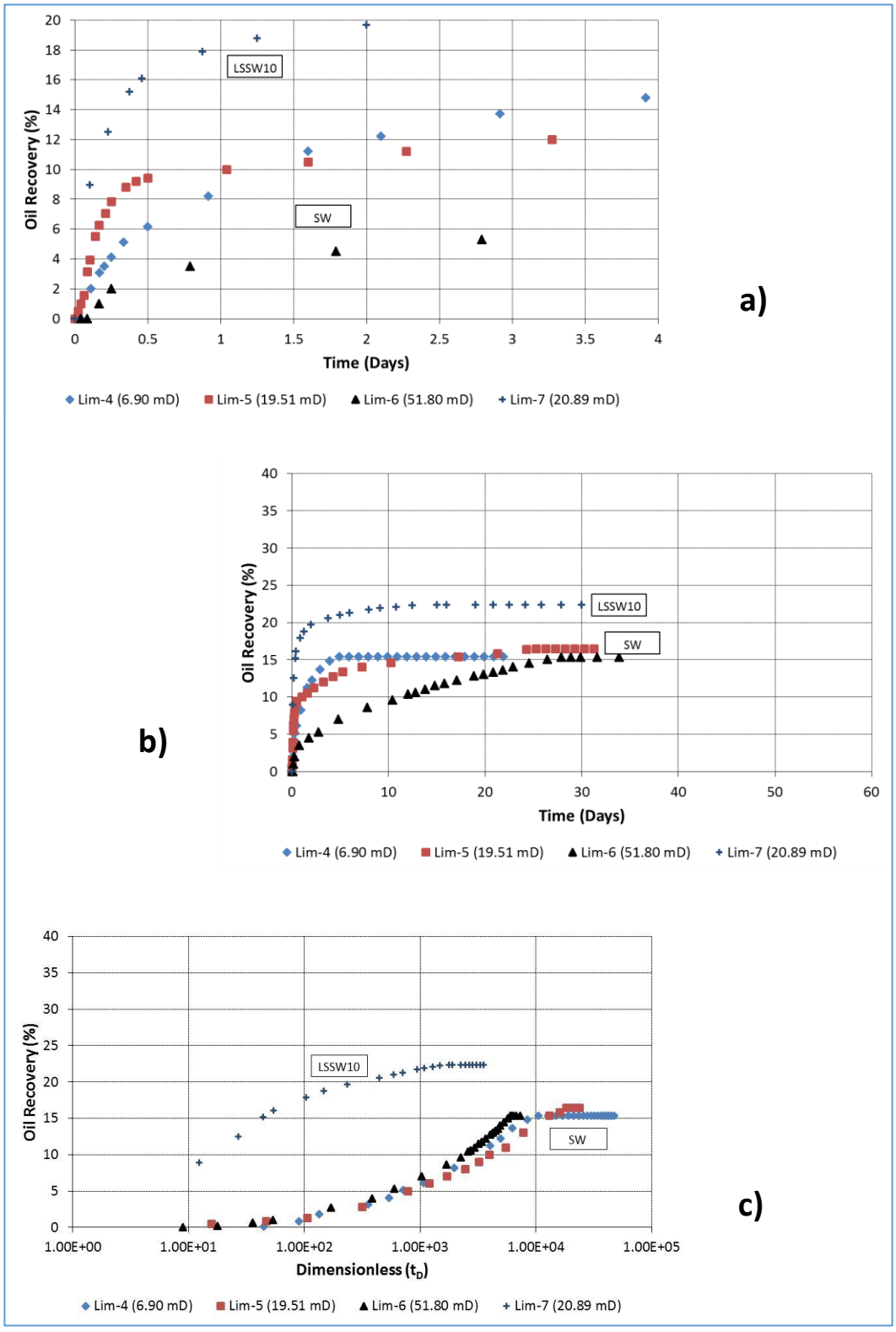

Figure 5.8: Oil recovery by spontaneous imbibition of smart waters into limestone cores, a) curves for early times, b) the whole imbibition curves and c) dimensionless imbibition time using a specific characteristic length.

For dolomite, the highest permeability cores yielded the fastest recovery at early time, when the seawater is considered as the imbibing fluid. The recovery curves for the dolomite cores are shown in Figures 5.9a, 5.9b and 5.9c. The trend in oil production behaviour differs from that indicated for limestone cores. In this case, all three dolomites imbibed faster than the limestone cores and initially, the recovery rate was greater (Figure 5.9a). For the first few days, the cores contacted with seawater all showed similar behaviour, but a much larger oil fraction was eventually recovered from the core with higher permeability. The core Dolom-1 recovered around 14 % of original oil in place (OOIP); however, this was lower than that obtained from the core Dolom-2, from which around 30 % was recovered, as shown in Figure 5.9b. The rate of imbibition increased with increasing permeability. In contrast, using a different imbibing fluid (LSSW10), it was observed that the lowest permeability core produced more oil at a faster rate, as shown in Figure 5.9b. However, comparison of the final oil recovery vs. permeability for the dolomite cores contacted with seawater showed a tendency for oil recovery to increase with increase in permeability. From the experimental observations of the dolomite cores, it can be seen that the permeability appears to be a dominant factor

The application of the equation approach of Ma et al. (1997) provided a satisfactory correlation of spontaneous imbibition results for limestone cores but not for the dolomite cases. Seawater did not change the initial wettability for two types of carbonate samples, except for one dolomite core which was affected by this fluid. However, the diluted version of seawater brought about a change in wettability for both rocks. Hence, this imbibing fluid forced the oil out of the pores, even with lower permeability. The results in this research are in good agreement with the observations reported by Mattax and al. (1962), Al-Lawati et al. (1996) and Tong et al. (2001).

During those experiments, oil droplets were observed to exit from all faces of the cores. Figure 5.10 illustrates the imbibition experiments with both types of rock. The upper faces of the cores reveal accumulation of oil in larger drops, and also that oil was expelled from the lateral sides of the cores. In general, the oil drops covered the whole core except for the areas where the surfaces were compact.

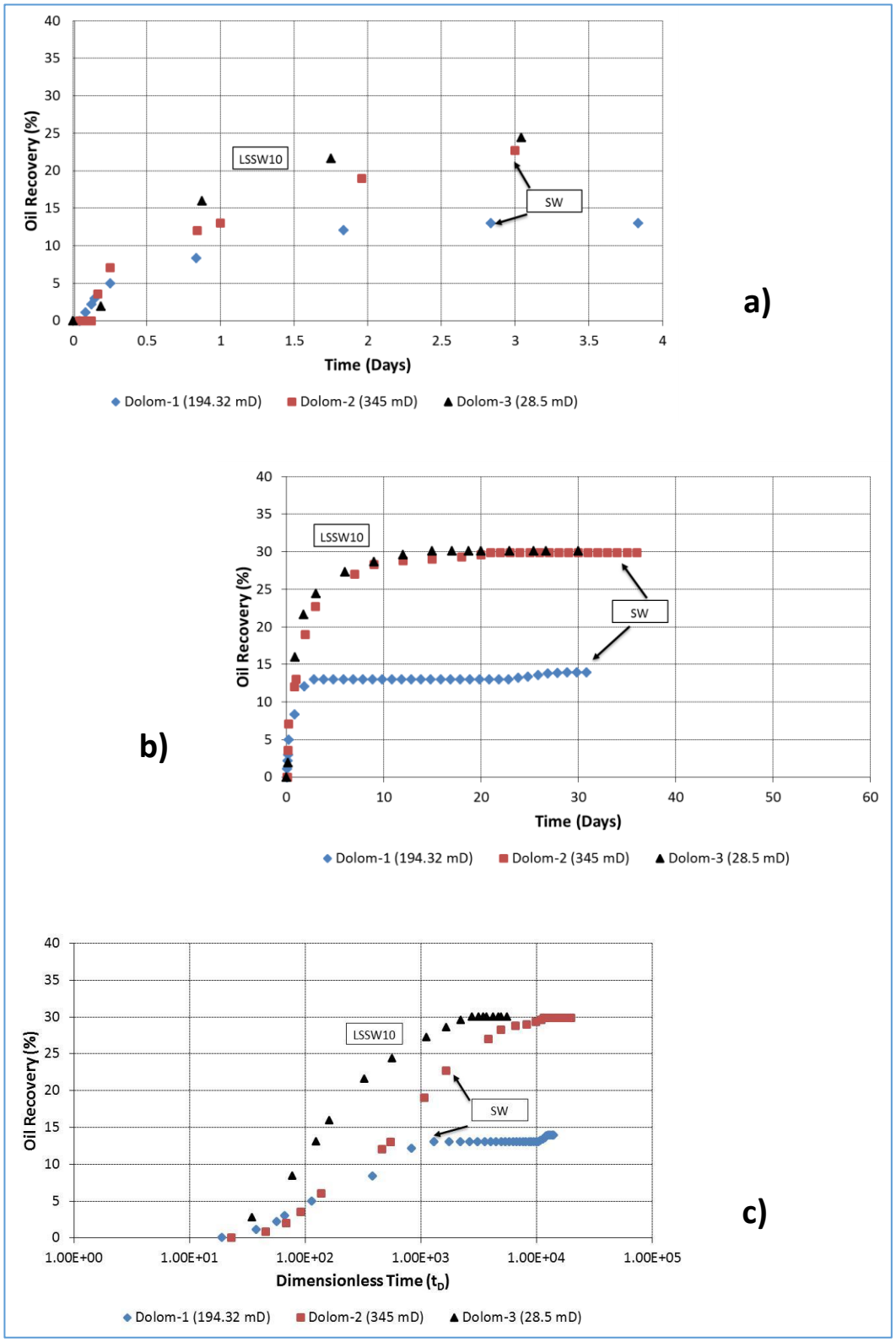

Figure 5.9: Oil recovery by spontaneous imbibition of smart waters into dolomite cores, a) curves for early times, b) the whole imbibition curves and c) dimensionless imbibition time using a specific characteristic length.

For carbonates, it has been well documented that seawater is able to improve the water systems to water-wet conditions at high temperature (Austad et al., 2005 and 2007 and RezaeiDoust, 2009). The conditions for obtaining improved water-wet systems by using seawater in carbonates are described as: 1) the injected water must contain SO_4^{2-} in addition to either Ca^{2+} or Mg^{2+} or both and 2) a high temperature, usually, >90^{o} C. So, one would expect to have good recovery factors based on both the stated conditions and the published results; however, the results were not completely consistent. In addition, most of the laboratory tests on smart water injection have been conducted with light oils or acidic oils. The experimental results showed that the crude oil interacted differently with the same rocks and the same imbibing fluids. The cores showed a favourable response to both fluids, principally to the low salinity water. The final oil recoveries of spontaneous imbibition tests by smart fluids were less than 30 %, which can be considered unattractive. Nonetheless, the tests using smart waters confirm the improvement of oil recovery.

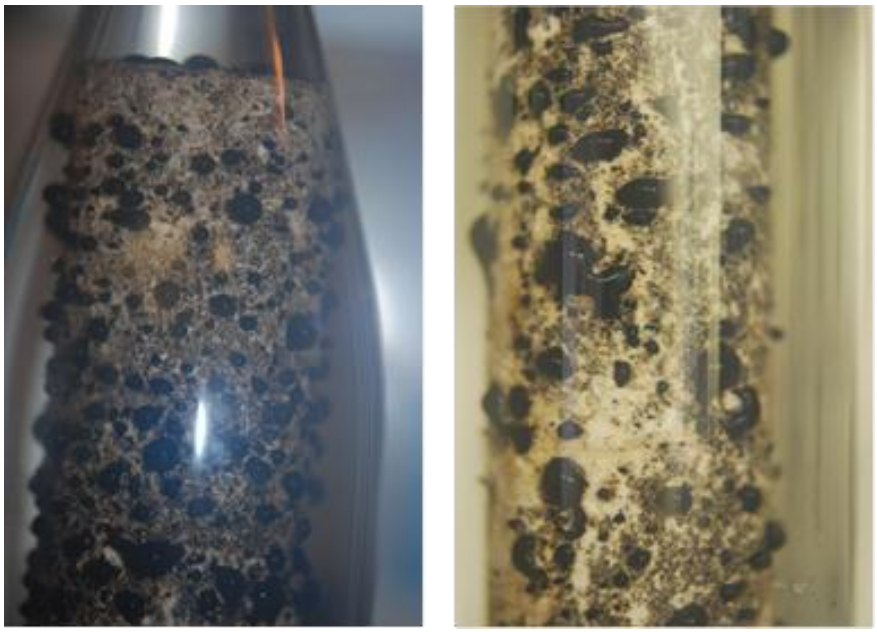

Figure 5.10: Cores producing oil in contact with seawater: limestone core (left side) and dolomite (right side).

To monitor a possible interchange of ions during the spontaneous imbibition (SI) tests, samples of the brines were collected and analysed before and after contact with the cores. Original composition and composition at the end of the tests are presented in

Figures 5.11a and 5.11b. For the experiments using seawater as smart fluid, the variation of the concentrations was unremarkable for most ions, except in the case of calcium and sulphur, where a rise was more noticeable. These variations may be related to the imbibing fluid/rock interaction. The analysis also reported small variations of magnesium and bicarbonates. These higher concentrations cannot be properly attributed to dissolution of the rock.

The increase in concentration is probably caused by the long period of contact with the imbibing fluids in the external faces of cores rather than the dissolution effect. The divalent ions (calcium, magnesium and sulphate) were not effective with seawater as an imbibing fluid, which could be viewed as almost contradictory.

However, previous experiments (Austad et al., 2005-2007; Fathi et al., 2011; RezaeiDoust et al., 2009; Tweheyo et al., 2006) indicated that the sulphur, calcium and magnesium were more active at high temperatures, leading to wettability changes and, hence, better oil recoveries.

When LSSW10 was used as an imbibing fluid, small concentrations of sulphur, magnesium and calcium were also detected in the imbibing fluid after the imbibition process. pH values after the imbibition process are shown in the Table 5.3. In general, these values remain stable.

Table 5.3: Changes in pH before and after the spontaneous imbibition processes for effluents.

Core Number	**pH (adim)**	**Imbibing Fluid**	**pH (adim)**
Lim-4	7.80	Seawater	7.91
Lim-5	7.80	Seawater	7.83
Lim-6	7.80	Seawater	7.90
Lim-7	7.20	LSSW10	7.38
Dolom-1	7.80	Seawater	7.71
Dolom-2	7.80	Seawater	7.78
Dolom-3	7.20	LSSW10	7.27

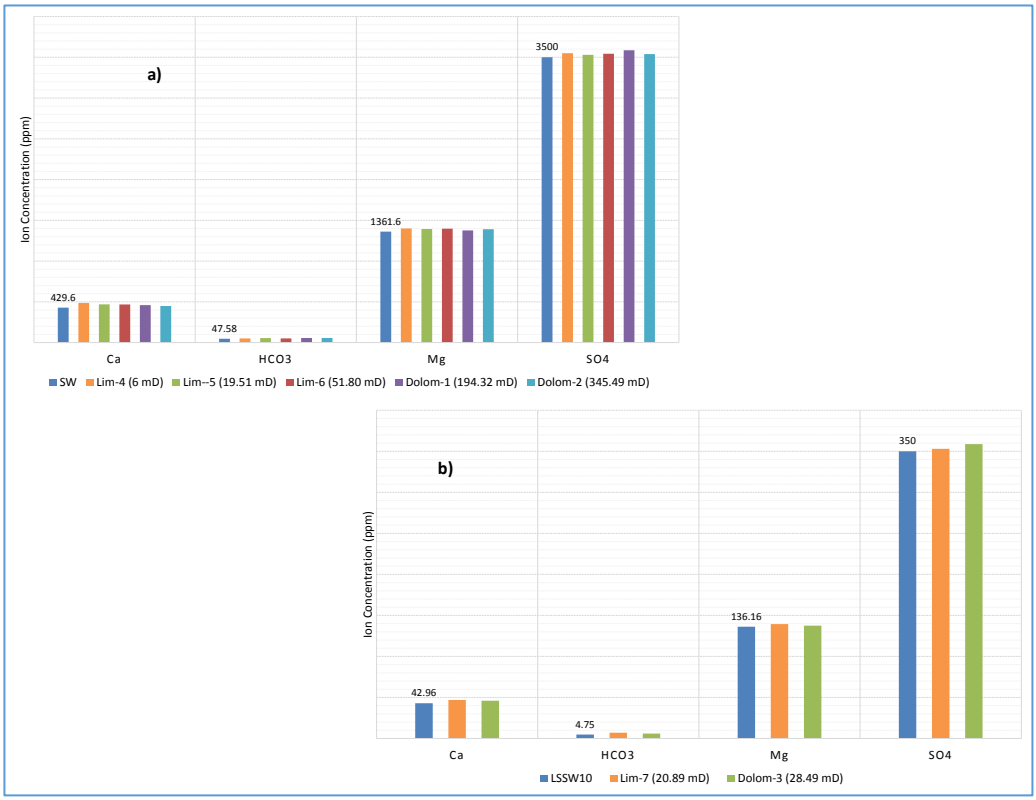

Figure 5.11: Changes in concentrations of ions when two different waters are used, a) seawater as imbibing fluid and b) low salinity seawater as imbibing fluid.

To explore the change in permeability, if it exists, the cores were cleaned, dried and saturated once again with formation water and the permeability values were then obtained. The measurements point to the absence of significant variations. The permeability values remained without changes. For instance, the permeabilities for Lim-4 and Lim-5 changed from 6.90 and 19.51 md to 7.01 and 19.45 md, respectively (Table 5.4). This is in good agreement with the pH results in Table 5.3 and with those shown previously in Table 4.4 in Chapter 4, where the brine/crude oil/rock systems hold pH values constant, to some extent.

Table 5.4: Changes of core permeability after the spontaneous imbibition processes.

Core Number	Initial k_{brine} (md)	S_{wi} (%)	Imbibing Fluid	RF (%)	Final k_{brine} (md)
Limestone					
Lim-4	6.90	31.17	Seawater	15.38	7.01
Lim-5	19.51	28.78	Seawater	16.47	19.45
Lim-6	51.80	31.57	Seawater	15.32	52.01
Lim-7	20.89	31.59	LSSW10	22.34	21.12
Dolomite					
Dolom-1	194.32	36.89	Seawater	13.95	193.01
Dolom-2	345.49	34.30	Seawater	29.84	343.98
Dolom-3	28.49	31.69	LSSW10	30.08	29.01

It is therefore concluded that seawater does not promote a wettability alteration for this basic crude oil in the presence of two types of rocks and fluids. Dissolution was not present as an effect, either.

5.4 FORCED IMBIBITION TESTS

As a part of the project of this research, a novel high pressure and high temperature setup was designed in-house to facilitate coreflood experiments (up to 150^{o} C and 10,000 psi). The schematic diagram of the setup used in this subsection is shown in Figure 5.12. The temperature-controlled oven houses all the lines, cells with injection fluids, transducers, the core holder and additional instruments.

In the tests in this study, the orientation of all cores was horizontal and they were maintained at approximately the same overburden pressure (OB) during the whole evaluation, as described in Chapter 3, subsection 3.3.4. Transducers and pumps were verified internally and calibrated, if it was necessary, before the start of each coreflood experiment. A pair of pumps was used for controlling the brine cells. and another pair of pumps for controlling the pressure in the oil cells, while one more pair of pumps was used for the overburden pressure and back pressure regulator (BPR). Note that, for these

experiments, the brine cells contain specific working fluids, and the oil cell contains extra-heavy crude oil.

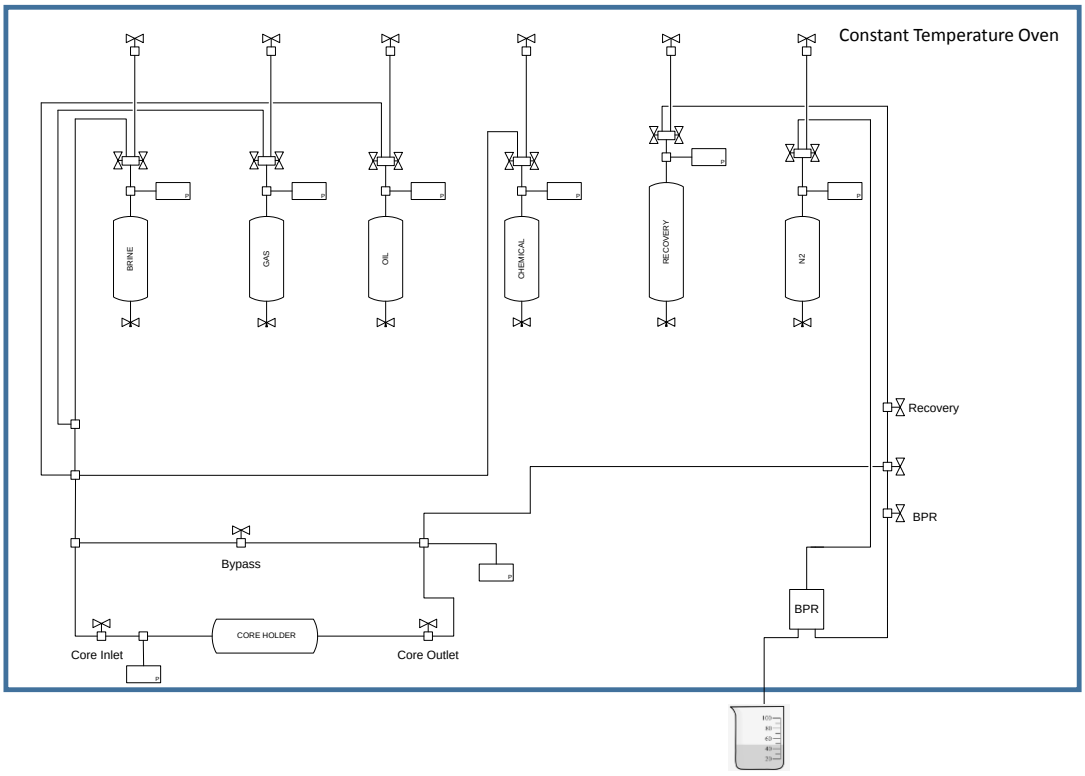

Figure 5.12: Simplified diagram of the high pressure and high temperature coreflood setup used in this research.

The procedure for preparation of each coreflood experiment was as follows:

-The coreholder was placed in the oven. If fluid samples were collected externally through the back pressure regulator (BPR), a stand and a conical test tube were used and located on the outside of the oven.

-Once the OB was at the working pressure, the inlet valve from coreholder was shut and the outlet valve was completely opened. The brine cells and the coreholder were not in direct communication: they were isolated from each other during the temperature variation. The oven was then turned on. The system started working at an initial working temperature of 30^{o} C.

-The internal pressure in the coreholder and cells was constantly monitored. Once all pumps were perfectly stable, the temperature was increased in increments of 5 degrees

Celsius. As the fluids expanded due to the change of temperature, they were automatically expelled from the coreholder via the BPR. The fluids were collected using the test tube outside the oven. The increments in temperature were gradually repeated until reaching the test temperature.

-Once the system was stable at test temperature, the pumps were stopped except those controlling the OB.

-The crude oil was injected through the coreholder for some minutes, then the offset for the system was taken. Subsequently, the injection of crude oil was continued and kept at very low rate in order to get the end points for the relative permeability curves when the differential pressure was stabilised. Pressure was monitored and the fluids from the core were also collected. When the aging time was finished (~20 days), the crude oil injection was ended.

-The brine cells were opened and brine flowed through the bypass. After some minutes, the injection was stopped and a new offset was taken.

-The coreflood experiment was conducted by injecting the working brine. During the experiment, crude oil and brines were centrifuged and separated.

-The pH and effluent composition of the produced water were constantly monitored. The pressure behaviour was also evaluated. Flow rate depended on the type of core, its characteristics and oil properties. The injection continued until the maximum oil was obtained.

Eight tests were carried out. In all of them, when the oil production stopped a change in the injection rate was applied to make sure that there was no more mobile oil. The oil volume (expressed as a percentage of the original oil in place) was measured as a function of pore volume injected. The experiments confirmed additional oil recovery when smart fluids were injected in both secondary and tertiary mode. Some tests had an additional coreflood experiment in order to evaluate the repeatability of the results. They were consistent with the first estimations.

When the coreflood experiment was finished, the core was then cleaned with appropriate solvents (toluene or methanol) for removing organic material and residual water at high temperature.

5.4.1 Coreflood Experiments with Limestone Cores

5.4.1.1 Effect of the Injection Mode for the Oil Recovery

Seawater was first injected as a secondary process and then low salinity seawater for a tertiary process (Limestone core 8). The total recovery factor was 52.09 % and 36.81 % using seawater and 15.28 % with LSSW10. The pH of the effluent also was measured at regular intervals after the effluents were collected. The values are indicated in Figure 5.13. The pH values stayed constant during the rest of the injection with seawater. It is also interesting to observe that for the tertiary program, the pH values increased gradually up to 7.4. The increase in oil recovery by LSSW cannot be attributed to this perceptible change in pH.

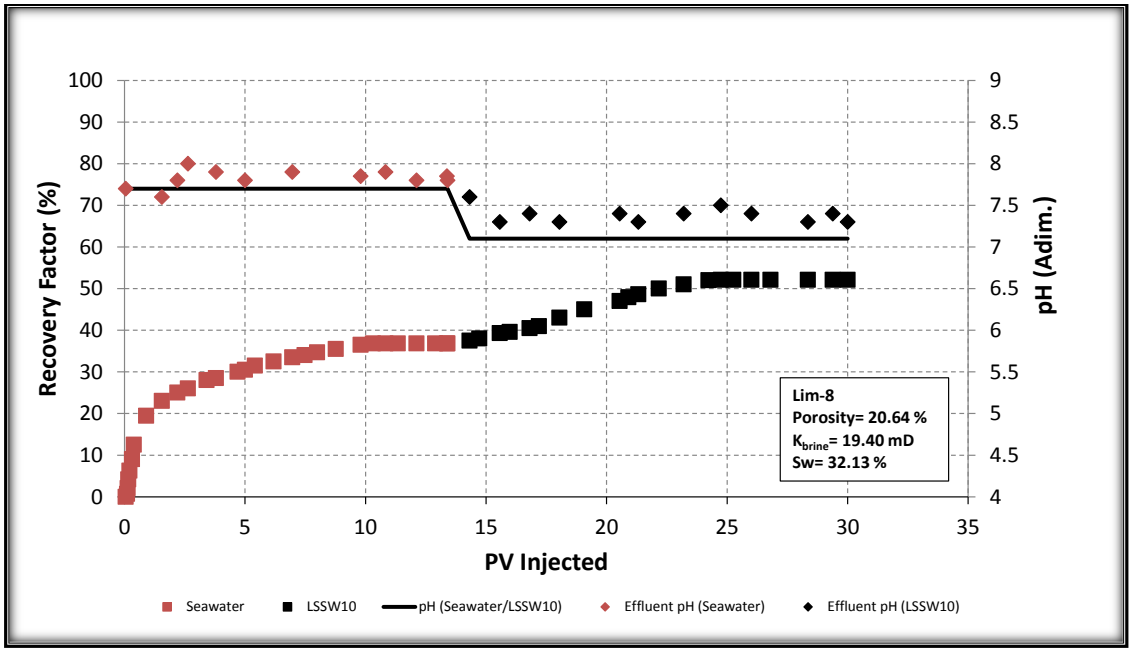

Figure 5.13: Oil recovery and pH versus pore volumes of injected fluids during both secondary and tertiary processes.

The concentration profiles of sulphate (SO_4^{2-}), magnesium (Mg^{2+}) and calcium (Ca^{2+}) in the effluent underwent variations. For instance, SO_4^{2-} and Mg^{2+} decreased in concentration a little; however, there was a constant production of Ca^{2+} and HCO_3^- during all of the experimental seawater injection, as shown in Figure 5.14. Mg^{2+} and SO_4^{2-} decreased as Ca^{2+} increased. The broken lines are the ions analysed from the effluents. Zhang et al. reported (2007) an increase in the effluent calcium concentration during seawater experiments at high temperatures. This reaction was interpreted as a result of substitution of certain ions on the internal rock surface.

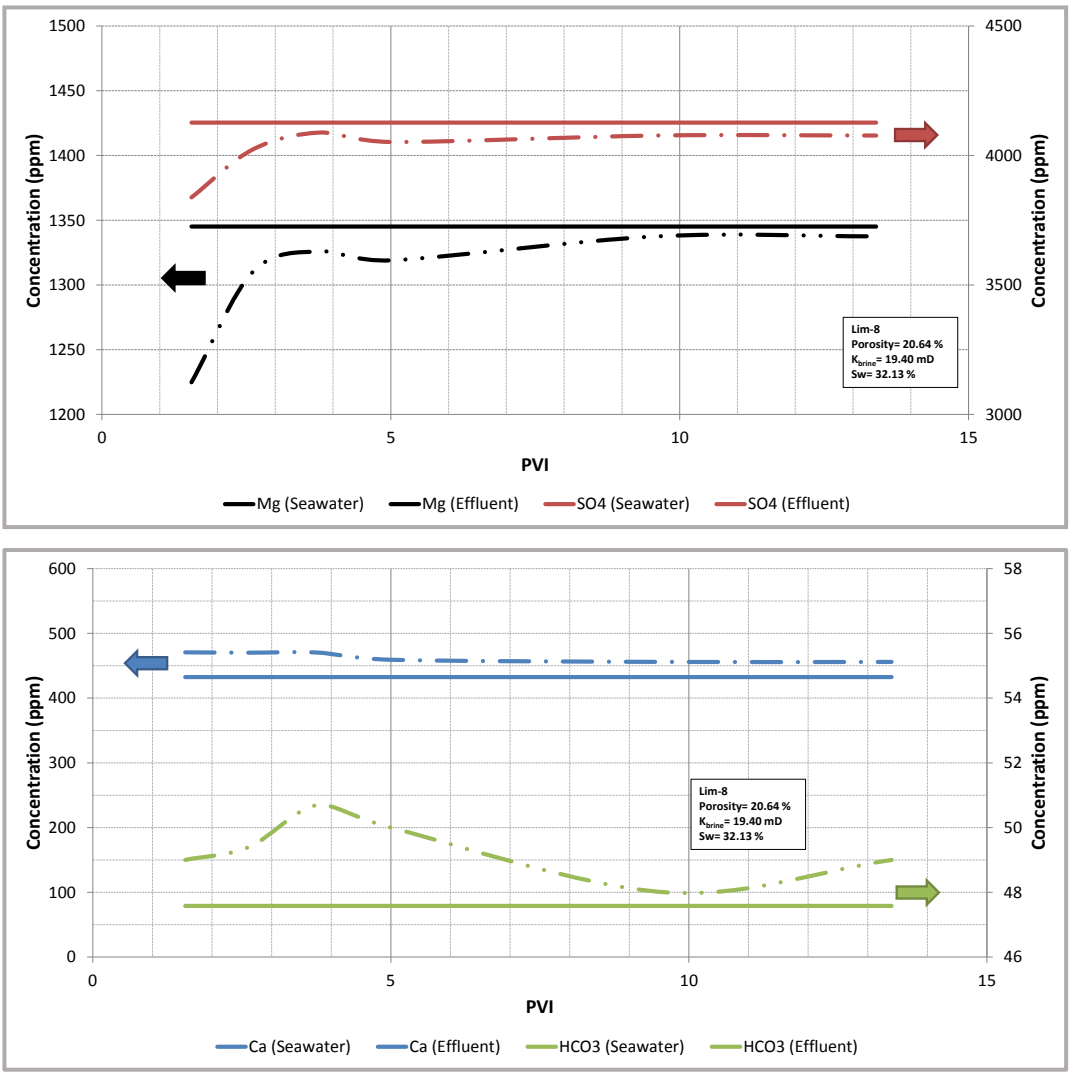

Figure 5.14: Changes in concentrations of ions when flooding seawater through Lim-8 at 92^o C.

In such a case, the results in Figure 5.14 may confirm this kind of substitution of ions as well. For this experiment, the influence becomes more pronounced and may represent one explanation of the effect attributed to the reactivity of key ions that have the capability of improving oil recovery. Thus, SO_4^{2-}, $Mg^{2+}$and Ca^{2+} turned out to be more reactive with these cores at high temperature, but the oil recovery was low in terms of the impact of the seawater injection.

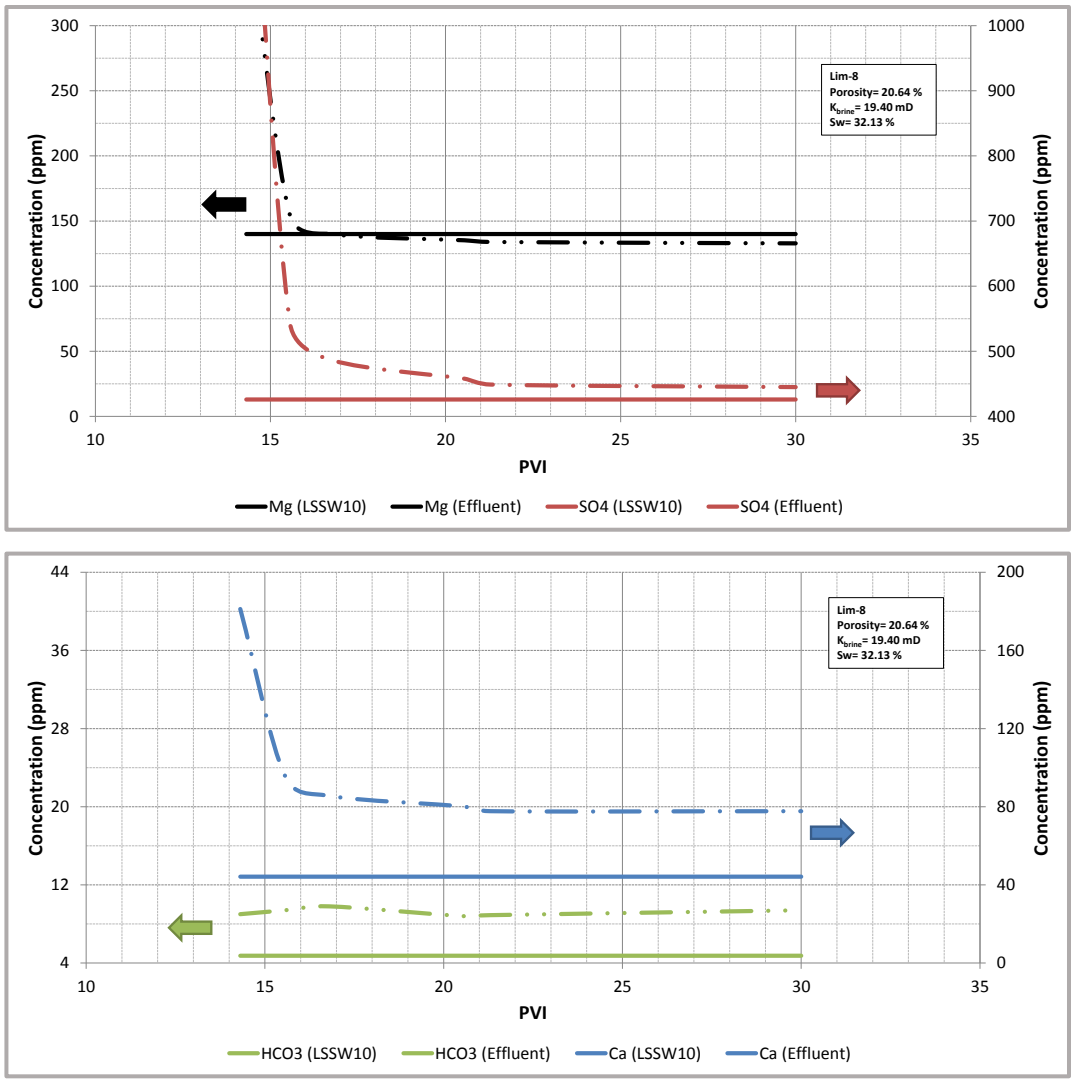

Figure 5.15: Changes in concentrations of ions when flooding low salinity seawater through the Limestone core 8 at 92^{o} C.

For the second part of the experiment, the behaviour of the concentrations changed (tertiary injection). The ion concentrations at the beginning of the low salinity injection

were higher than those injected and this meant that effluents of the first pore volumes appeared to have a mix of brines, seawater and low salinity seawater. Later, the concentrations of calcium, bicarbonate and sulphate were slightly higher than injected concentrations (Figure 5.15), in contrast, the magnesium, chloride and sodium concentrations stayed constant. The potassium concentration was unchanged throughout the whole experiment. As described, during the course of the injection pH was monitored in the effluents. In this experiment a pH increase occurred for the tertiary process.

Another coreflood experiment was conducted at 92^{o} C reusing the previous core. Notice that the permeability was measured after the previous experiment. The value underwent a modification, changing from 19.40 to 21.80 md. This modification is in good agreement with the variations of measured calcium and bicarbonate ions. For this experiment, a diluted version of seawater was also flooded through the core, as a secondary process. The LSSW10 injection resulted in the final recovery of 62.91 % OOIP. After the low salinity injection, seawater was injected but did not result in significant production, as seen in Figure 5.16. Once again, the pH showed variations for both processes. On the one hand, the pH increased from ~7.2 to ~7.7 for the first period. These values are close to the value previously calculated in subsection 4.3.1.2 (pH ~ 7.87).

Oil was not observed when the injection rate was increased. After switching to seawater, the pH remained at about 7.6, due to the difference in the concentration of ions between LSSW10 and SW. No extra oil was recovered after SW injection. In both experiments with the same core, the response in the rise in pH during the secondary processes may be caused by the reaction between the rock and the composition of the injected brine. Effluents were collected for ion analysis. After 5 pore volumes, the equilibrium was assumed to be reached and the effluents' pH and ionic composition were also assumed to be representative of the injected brine. When no more oil was produced by LSSW10 injection, pH stabilized, whereas ion concentrations had curious variations composed of irregular increases and decreases.

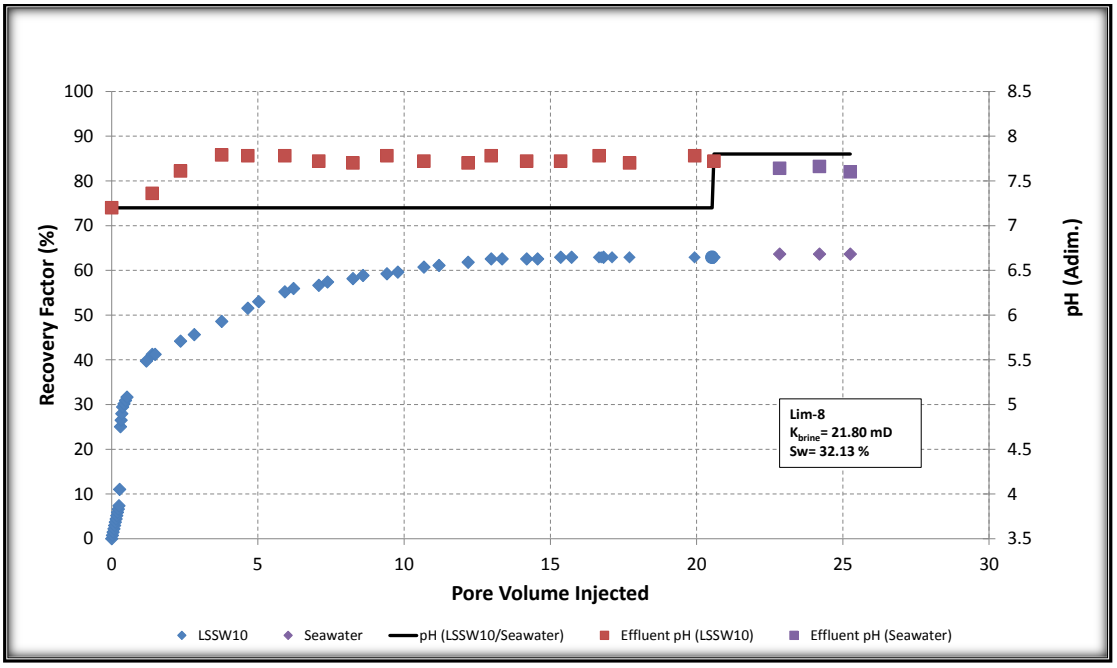

Figure 5.16: Cumulative oil recovery at two stages of injection with smart waters at 92^{o} C.

Flooding the core with low salinity seawater concentrations of the potential determining ions indicated the possible liberation of such ions. Figure 5.17 depicts results for the same core, where certain ions suffered variations in concentration. For this experiment, low salinity seawater was injected as a secondary process. The concentration of magnesium became constant and that of sulphate became slightly higher than the original value. Concentration of calcium and bicarbonates in the effluents increased to twice their initial concentrations.

The variations continued for more than 5 pore volumes and could indicate, for this case with low salinity seawater, that these two ions are being released by the core. Potassium, sodium and chloride concentrations remained more or less stable. From 13 to 20.6 pore volumes injected no more oil production was gained for this experiment, under the secondary method; however, important changes in ionic concentrations were detected.

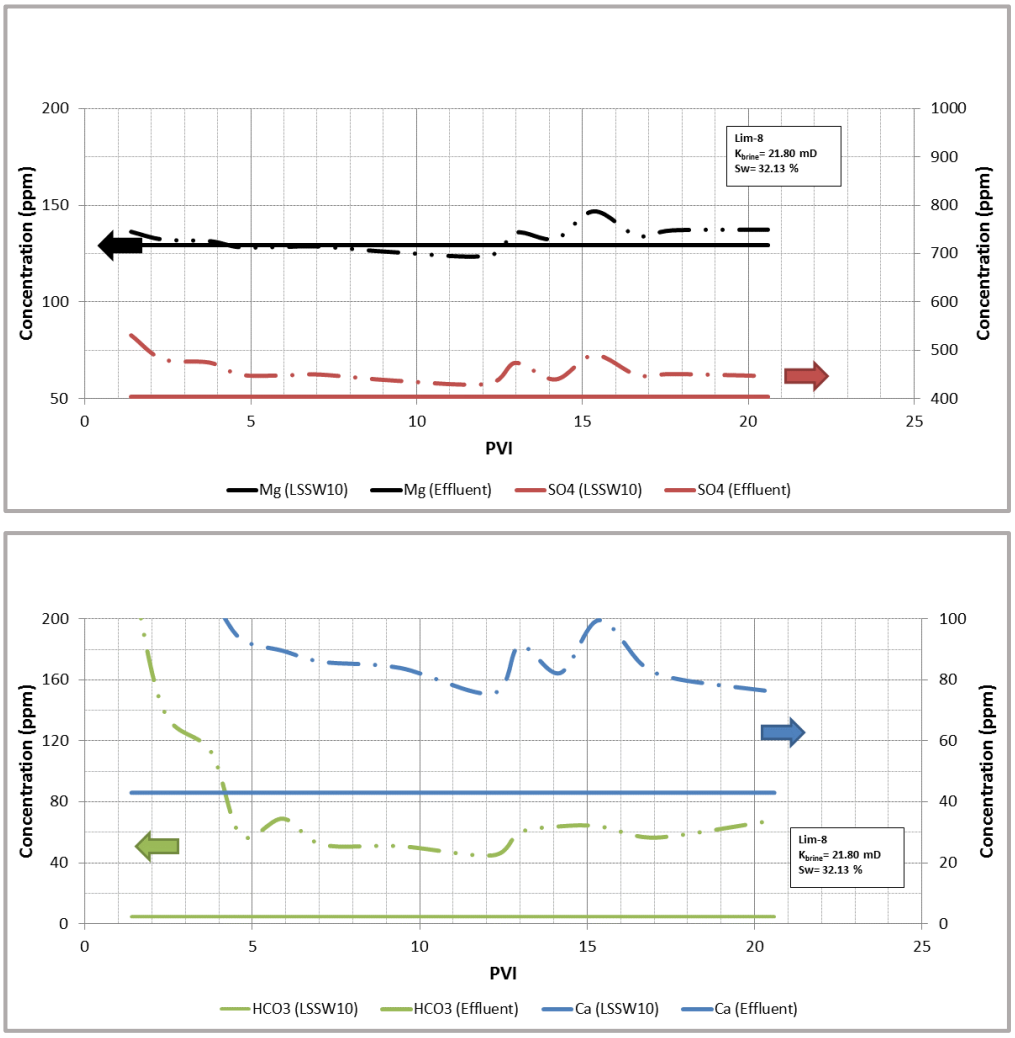

Figure 5.17: Variations in ions concentrations during low salinity water injection.

One could generalise that such a variation of ion concentrations in the effluents yields extra oil under low salinity injection. This generalisation may be adapted as a working hypothesis for the coming experiment. Once the experiment was finished, solvents were used to clean the core, then formation water was injected to measure the permeability. The value of permeability fluctuated around 25.8 md.

The jump in the value may be attributed to the dissolution of the rock due to the interaction between the basic crude oil and the brine, which is generating *acidic water*, as described in Chapter 4.

5.4.1.2 Effect of Rock Dissolution on Oil Recovery

In order to validate if the rock dissolution is taking part in the interactions in the experiments, the previous test was repeated using low salinity water as injection fluid. The LSSW10 injection turned out to show the same behaviour. During the injection, a period of shut-in (soak period) lasting approximately 24 hours (at 13.5 injected pore volumes) was performed to evaluate the functioning of the dissolution mechanism in heavy oils. An unexpected volume of oil was recovered during this time. This event is more clearly illustrated in Figure 5.18. This closed period could have created a new oil bank. Oil production increased from 61.72 to 67.98 % of original oil in place (OOIP). A rise in the rate was applied to make sure that there was no more mobile oil. A new closure was applied in order to validate the new findings. No extra oil was recovered. The pH of the LSSW10 started at around 7 and increased gradually to stabilize at approximately 7.8.

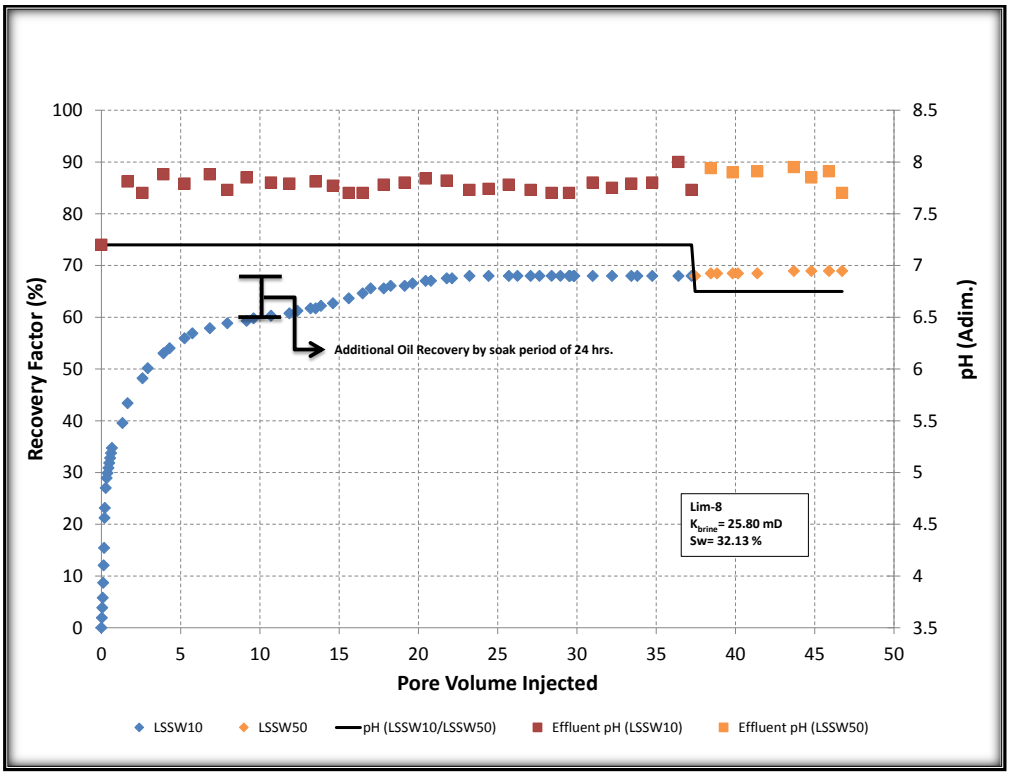

Figure 5.18: Oil recovery vs pore volume for the validation of the impact of dissolution.

Effluents were also taken and they were analysed. Based on Middle Eastern oil results (Yousef et al., 2010-2011-2012), a second diluted version of the seawater was considered for the tertiary method. This new version of low salinity water was made by reducing the ionic concentrations 50 times. Once again, the pH had variations. On the one hand, the pH increased from ~6.7 to ~7.9. The pH did not increase when the rate of injection was modified. Oil was not observed during these variations. On the other hand, after switching to LSSW diluted 50 times, some extra oil was recovered after injection of this new brine, ~1 % of OOIP. Thus, this new smart water did not result in significant production.

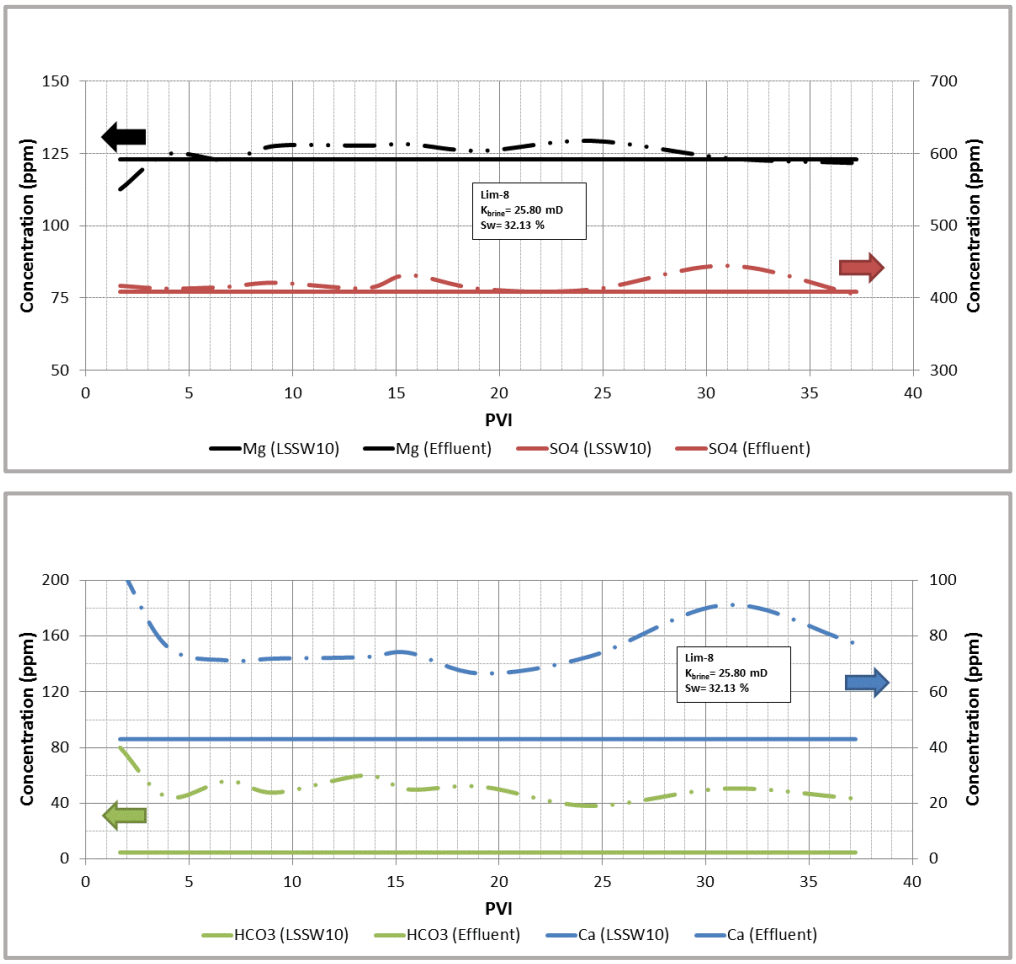

Figure 5.19: Presence of higher ion concentrations in effluents for the validation of the presence of dissolution of the core.

Figure 5.19 describes the variations in ion concentrations for this experiment. For magnesium and sulphate, no major variations in the concentrations occurred. Calcium rose to 2 times the original concentration and then remained stable at those values. Similar variations were observed for the bicarbonate concentrations. The core exposed to LSSW50 injection did indicate an increase in bicarbonate ions from the brine and at the same time an additional amount of calcium was produced by the core, as shown in Figure 5.20.

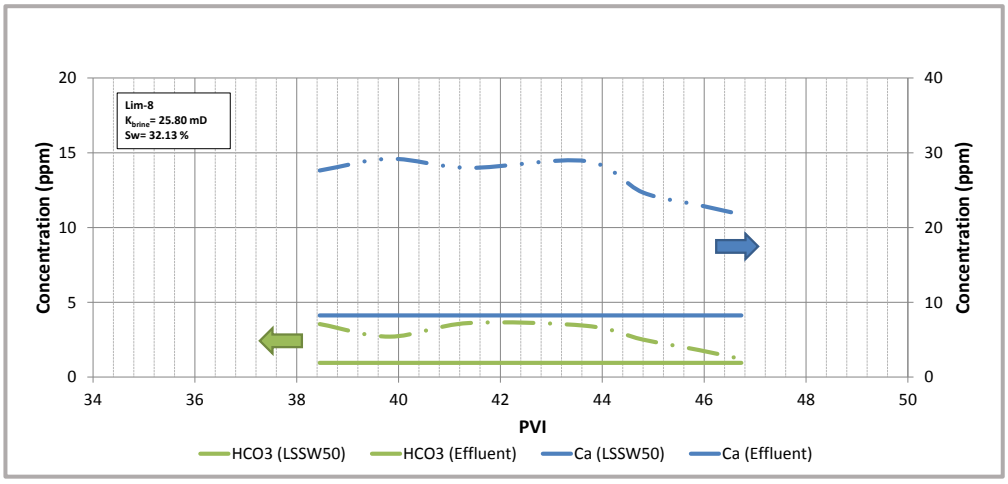

Figure 5.20: Chemical analysis results for Ca^{2+} and HCO_3^- in effluents for core flooded with LSSW50.

Figure 5.21 compares the differential pressure (DP) across the core for the last two experiments, in which LSSW10 brine was used. The behaviour of the DP is fairly similar to DP in the second injection, showing slightly higher values at soak times. It is observed that the DP during each shut-in period increases, due to the opening of the system induced by the start of the injection. Nevertheless, the pressure behaviour in each experiment is relatively similar, indicating stable profiles throughout the tests. These results show that the differential pressure analysis across the cores cannot be used for detecting or providing evidence of certain phenomena, such as dissolution. However, both the increase in calcium and bicarbonate in the effluent of the injected brine and the change in the permeability value corroborate the notion that dissolution is taking part and may influence oil recovery during coreflood experiments.

This demonstrates that the injected brine is capable of dissolving and transporting released material from the core which is not detectable in the pressure behaviour throughout the core. The final permeability value was 30.92 md.

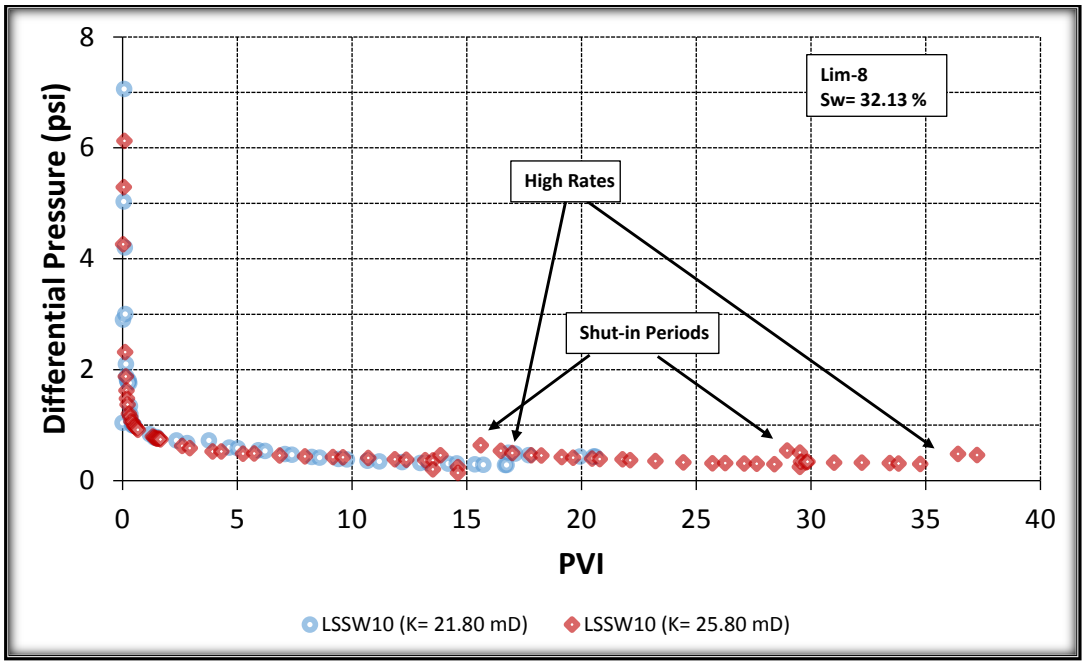

Figure 5.21: Differential pressure across core versus pore volumes for the Lim-8.

5.4.1.3 Additional Experiments

Before running the coreflood experiments with dolomite cores, another limestone core was chosen for running with seawater injection. In this case, the total amount of oil was 37.65 % OOIP (Figure 5.22). Overall, trends for the limestone cores, Figures 5.13 and 5.22, are in reasonable agreement with published literature findings. Zahid et al. (2012), Chandrasekhar et al. (2013) and Al-Hashim et al. (2015) provided similar results when seawater was used as a smart fluid for limestone cores.

The effluents were completely analysed for calcium, magnesium, sulphur, chloride, sodium, bicarbonates, potassium and possible traces of strontium. The results showed that concentrations of Ca^{2+} and HCO_3^- increased a little, whilst those of Mg^{2+} and S^{2-} dropped in the effluents. Chloride, potassium and sodium remained stable. Minimum traces of other ions were not significant. These outcomes are in line with previous

studies. The impact on the oil recovery based on the pH and the variation of the effluents was analysed. However, the pH did not show a perceptible change. In general, the concentration of calcium and bicarbonate remained consistent in its rise during the whole experiment.

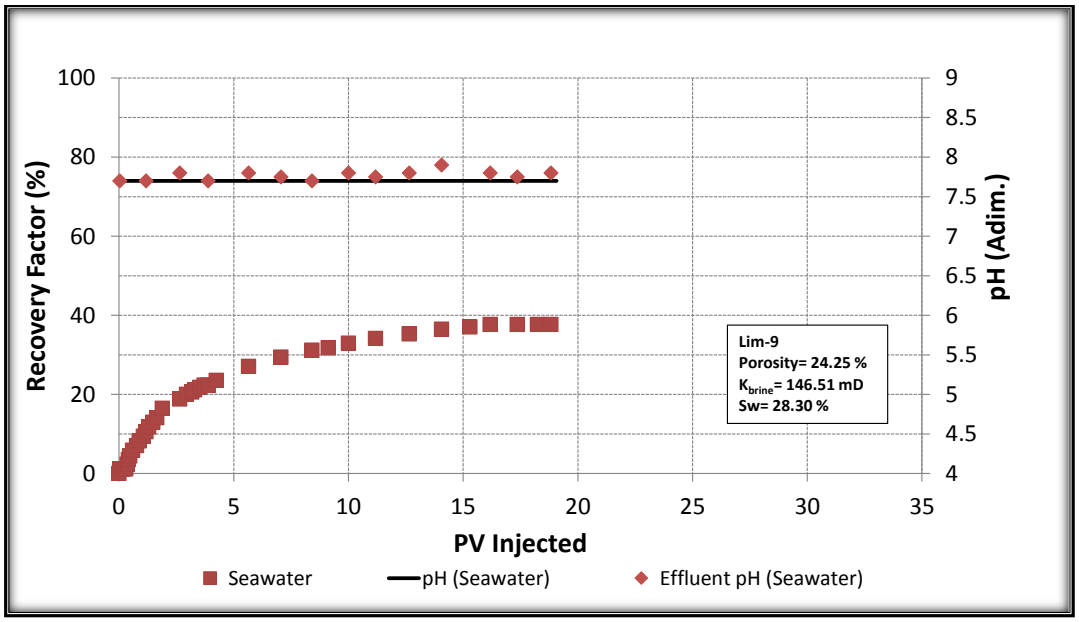

Figure 5.22: Cumulative oil recovery for another limestone core with seawater at 92° C.

Table 5.5 lists both initial and final permeability values for all coreflood experiments. The results of permeability changes are shown as a function of the injected fluid. Although calcium and bicarbonates ions increase moderately, triggering a rise in the permeability, in the final results for the low salinity seawater, an opposite value is observed to that of seawater. At first glance, the seawater result is in good agreement with that in subsection 4.3.1.1, where its saturation index was positive, implying that the brine is supersaturated and may precipitate as temperature increases. In this specific case, small changes occurred in the effluent composition, leading to production of certain ions and absence of others. Probably, some calcium and bicarbonate ions were less soluble, creating damage which was generated by the injection of this brine and this was finally confirmed by the permeability measurements.

Table 5.5: Changes of core permeability after the coreflood experiments.

Core Number	Initial k_{brine} (md)	Process	Injected Fluid	RF (%)	Final k_{brine} (md)
Lim-8	19.40	Secondary/Tertiary	Seawater/LSSW10	52.08	21.80
Lim-8	21.80	Secondary/Tertiary	LSSW10/Seawater	63.65	25.80
Lim-8	25.80	Secondary/Tertiary	LSSW10/LSSW50	68.95	30.92
Lim-9	146.51	Secondary	Seawater	37.65	121.43

5.4.2 Coreflood Experiments with Dolomite Cores

5.4.2.1 Effect of the Injection Mode for the Oil Recovery

Dolomite core 4 (Dolom-4) was flooded with a diluted version of seawater (10 times) as a secondary process. Pressure, pH and effluent composition were constantly monitored (Figure 5.23). After 22 pore volumes were injected, a 24-hour soak period was applied. No extra oil was recovered after this closure. Because of the high permeability of the core, a high rate was applied at the end of each stage (20 cm^3/hr). The LSSW10 injection resulted in the final recovery of 69.30 % OOIP. With respect to pH, after rising slightly and staying stable during injection of 9.5 pore volume, it fell at 10 pore volumes injected and fluctuated between 7.2 to 7.3 units. On average, these values are slightly lower those found in Chapter 4, where static condition tests were performed.

For the effluents of the LSSW10 injection period (Figure 5.24), it may be clearly seen that the calcium and bicarbonate concentrations rose and those of sulphate and magnesium also exhibited small variations. The concentrations of the rest of the elements remained constant (sodium, potassium and chloride). Nevertheless, the behaviour during the coreflood experiment with both limestone and dolomite cores was very similar in terms of production of ions. This production may be linked to the reaction of the injected water, firstly with the crude oil and subsequently with the rock, leading to a possible dissolution effect. Later, this assumption was supported by the measurement of the new permeability, which turned out to be higher, 180.28 md. A tertiary programme was not applied for this test.

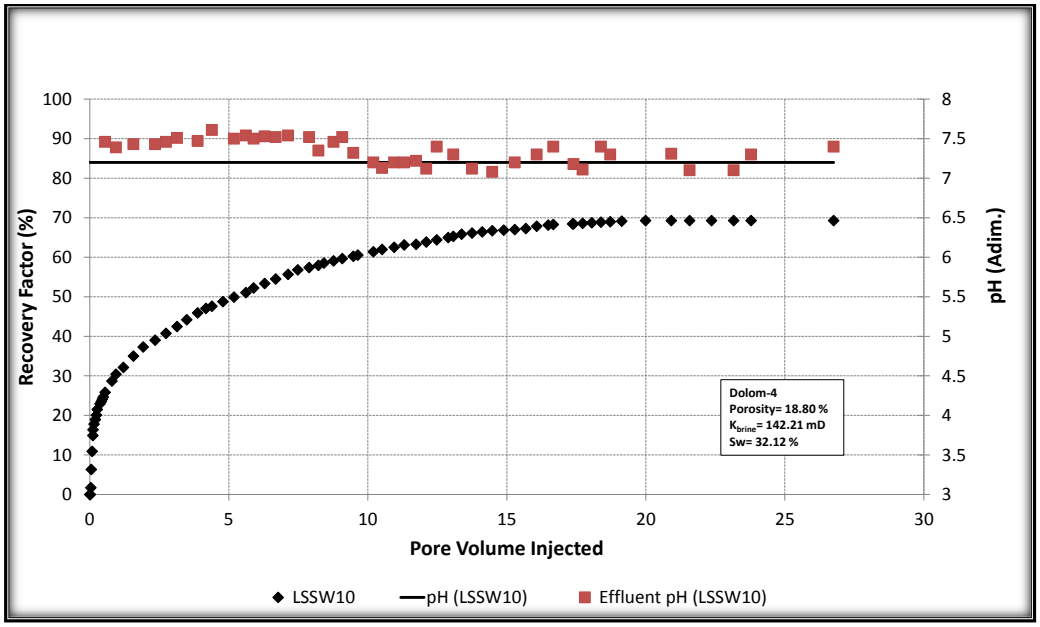

Figure 5.23: Cumulative oil recovery for a dolomite core with LSSW10 at 92° C.

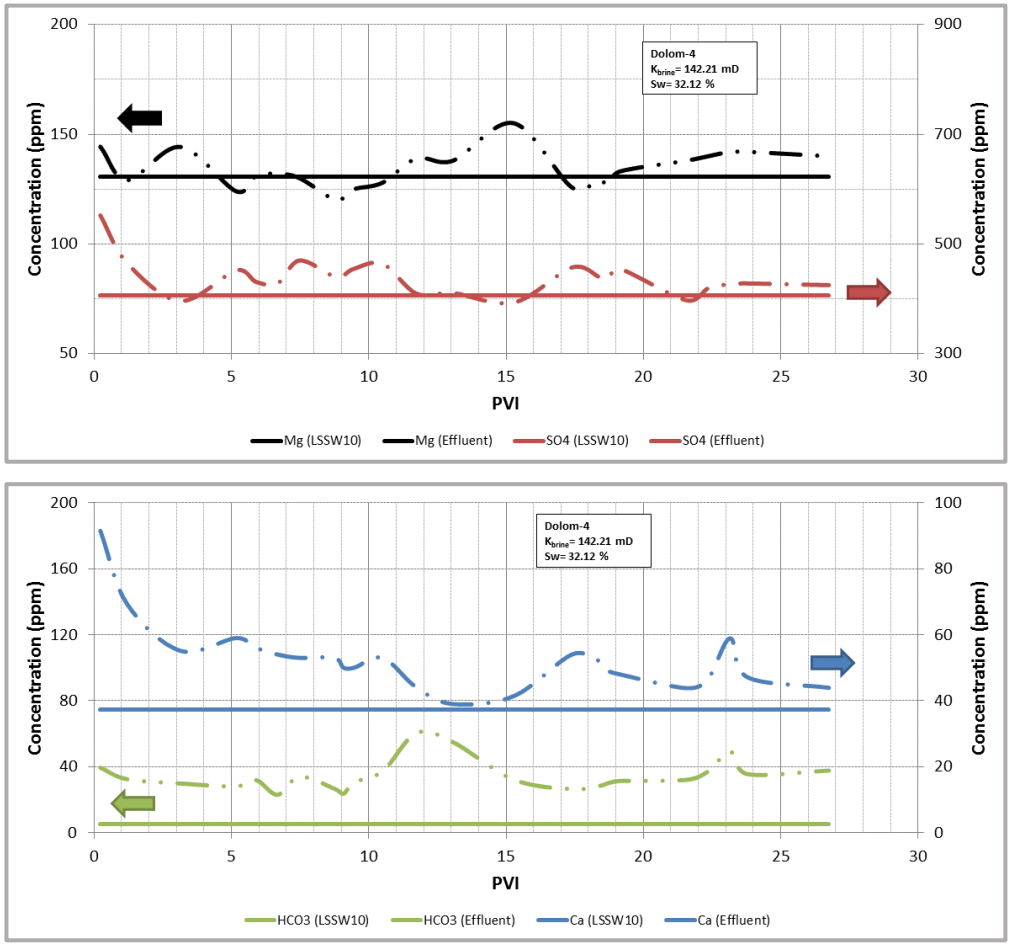

Figure 5.24: Changes in ion concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- when low salinity water is flooded through the Dolom-4 core at 92° C.

Once the experiment with low salinity seawater was finished, the core was cleaned and reused later. The same process was repeated, except the type of injected brine was changed. This time, the core was brought into contact with seawater. High oil volume was produced at early time. Before 4 pore volumes had been injected, the recovery factor was around 31 %, as shown in Figure 5.25. From 5 to 10 pore volumes, the recovered oil was around of 2 % more. Later, pH measurements were obtained from the effluents. The pH tended to drop from 7.8 to 7.0, approximately. This means there was a difference with respect to the limestone experiments, where there was a small rise for the pH values when seawater was injected as a secondary process. Although the contact angle measurements for this type of rock showed an alteration of the initial conditions of wettability from an intermediate-wet to water-wet system, the coreflood experiment results did not reveal such a modification, and thus a low oil recovery factor was not expected. Alotaibi et al. (2010) obtained similar results using dolomite cores at 90^{o} C. In their tests, the recovery factor was around 35.5 % after 2.5 pore volumes.

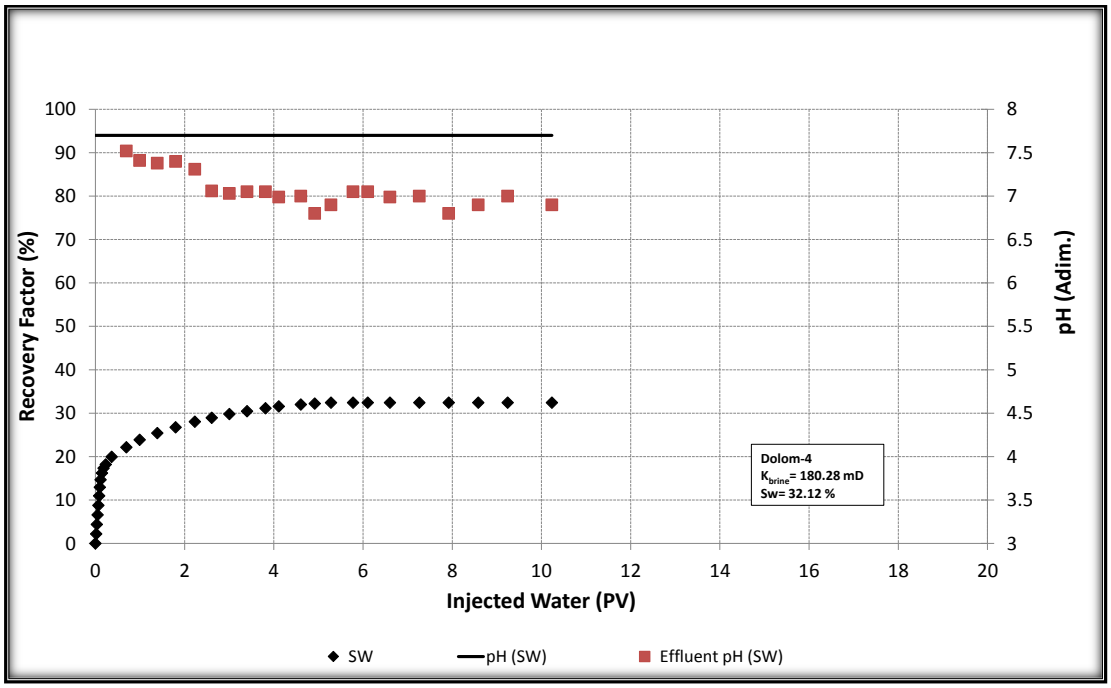

Figure 5.25: Oil recovery versus pore volumes of injected seawater at 92^{o} C.

The ion composition analysis of the effluents is different from that seen in the limestone cases. The reactivity of the core towards the divalent ions appeared to be negligible, except for magnesium. This divalent ion and also sulphur showed small variations on their concentrations, staying active at high temperature.

The bicarbonate ion was completely inert. Under conditions of high pressure and temperature, the system did not maintain a continuous production of calcium and bicarbonate ions as in previous experiments with limestone cores, as can be seen in Figure 5.26 below.

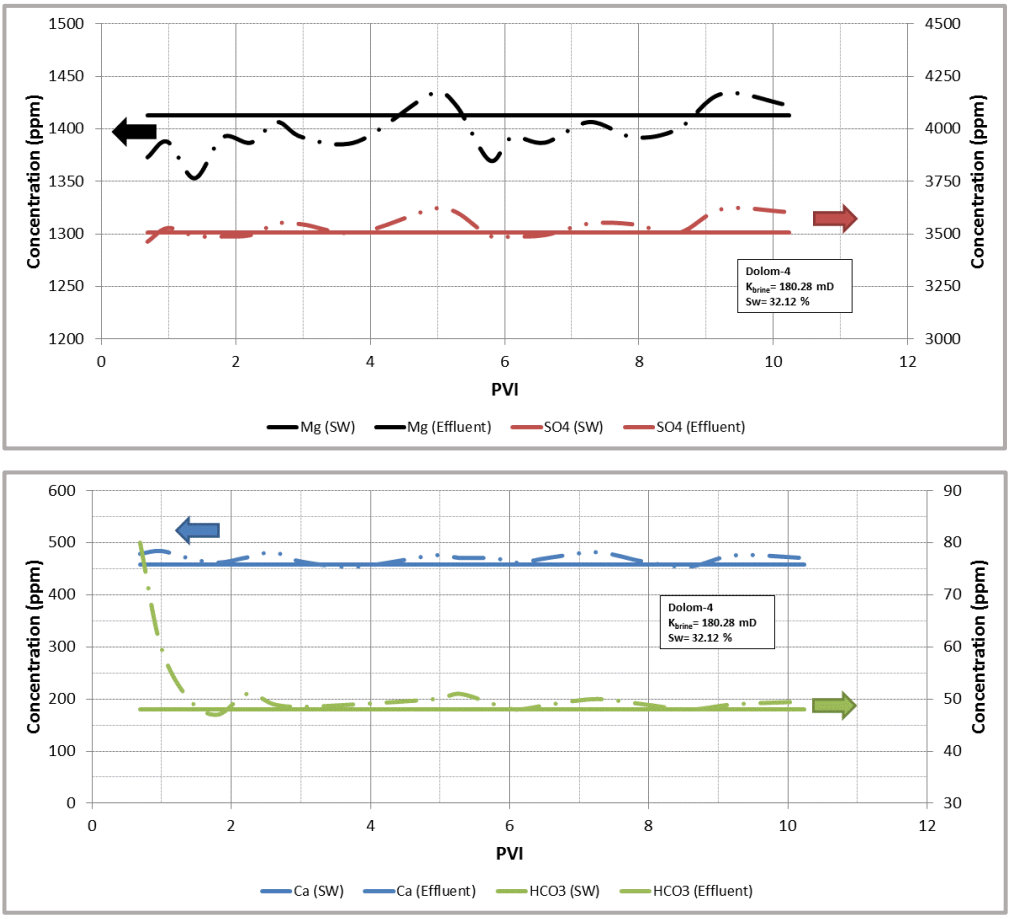

Figure 5.26: Changes in ion concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- when seawater is flooded through the Dolom-4 core at 92° C.

Calcium, magnesium and sulphate have been reported as potential determining ions for improving oil recovery in carbonate rocks. For this experiment, the effect of such ions on the wettability change is not in good agreement with the results described by Austad's group (2005-2007, and 2009-2011). However, there is a contrast between the ion evaluation and the permeability measurement after the experiment. The water permeability decreased dramatically to a stable value of 64.08 md, which was around 65 % below its initial permeability (180.28 md). The decrease in permeability denotes that the permeability was dominated by the damage resulting from the seawater injection. The lack of ion production and the loss of permeability may be linked to this damage caused by seawater injection. Notice that the damage is higher than that identified with the experiment for Lim-9, as shown in Table 5.5. Overall, these cores were found to suffer permeability loss when seawater is used as a smart fluid.

From the differential pressure curves in Figure 5.27, it is evident that during each experiment, the pressure first increased then decreased slowly, and later the trend was stabilised. In addition, from this Figure, some small variations of pressure were noticed when both high rates and shut-in periods were applied. Thereafter, other major changes in pressure were not detected or the differential pressure response did not give an indication of any instability and hence unusual behaviour.

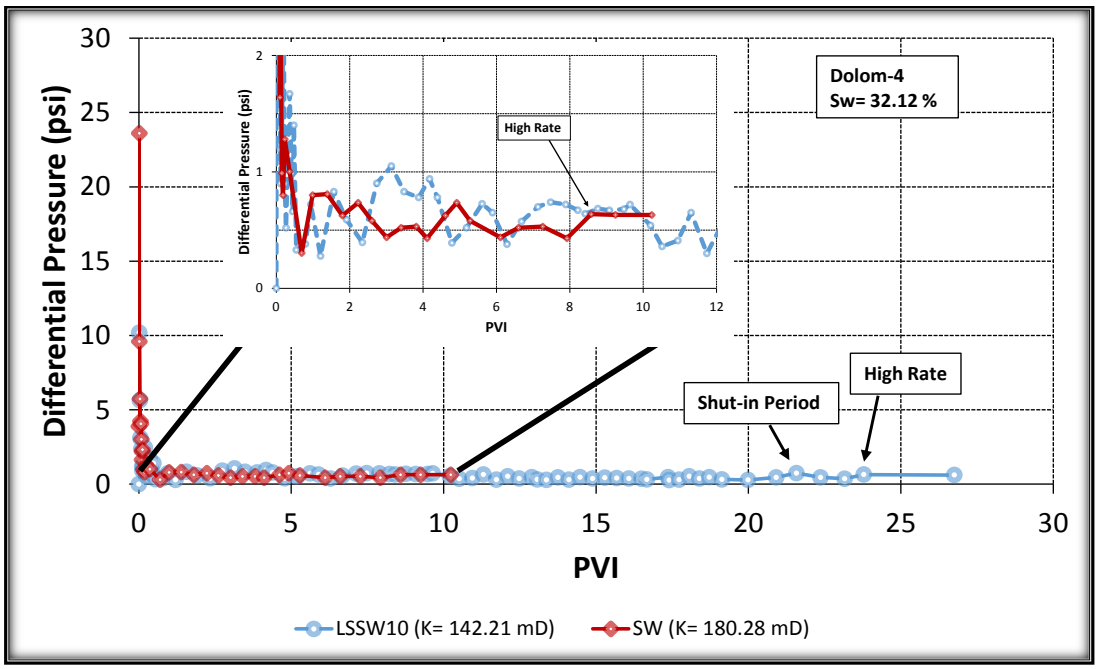

Figure 5.27: Differential pressure across core versus pore volumes for the Dolom-4 core with two brines.

For dolomites, the seawater was supersaturated (SI>0, Chapter 4, Table 4.2) at high temperatures. That is, more of the ions are in solution. This state of saturation set up the potential for high precipitation, gradual pore blocking (partial plugging) and finally loss of permeability (up to 65 % for the Dolom-4 core), as shown in Table 5.6. With limestone cores, seawater may still create precipitation but only a little (SI≥0, Chapter 4, Table 4.2), creating less damage or loss of permeability. As a result, it would cause no rapid precipitation, which is in good agreement with the result in the Table 5.5 for the Lim-9 core, where the permeability dropped by 20 %. If the saturation index is negative (SI<0), as for the low salinity waters shown in Table 4.2, then no precipitation will take place. Consequently, the low salinity waters may adequately dissolve and transport the released material from the rock, which originated from the action of the acidic water derived from the crude oil/low salinity brine interaction. In the limestone case, the magnesium and calcium may mostly act as inhibitors, because they are dissolved in the low salinity water (Morse and Arvidson, 2002). On the other hand, calcium could act as an inhibitor for dolomites (Zhang and al. 2007). Over the long term this process will lead to improving the internal conductivity in the porous media, generating a better permeability, as seen in Tables 5.5 and 5.6 for low salinity water injection (from 19.40 to 25.80 and 142.21 to 180.28 md, respectively).

Table 5.6: Changes of core permeability after the coreflood experiments.

Core Number	**Initial k_{brine} (md)**	**Process**	**Injected Fluid**	**RF (%)**	**Final k_{brine} (md)**
Dolom-4	142.21	Secondary	LSSW10	69.30	180.28
Dolom-4	180.28	Secondary	Seawater	32.43	64.08

5.4.2.2 Additional Experiments Using a Different Crude Oil

In order to verify that the oil recovery factor may be associated with the dissolution effect, other parallel coreflood experiments were conducted using the same core. In this case, the cores were saturated with crude oil “E”, which is more acidic. The results are plotted in Figure 5.28. For the first experiment with this crude oil, low salinity seawater was intentionally injected. The aim was to firstly remove the damage which existed. In the second case, seawater injection was first flooded as a secondary process then low

salinity water was injected. Only 42 % of OOIP was recovered during low salinity water injection as a secondary program. When the brine was changed to another low salinity water, LSSW50, an increase in oil production was noticed. After 10 PV were injected, the recovered oil exceeded 45 %. The effect of the low salinity water was less that that observed in the coreflood experiments for the basic crude oil, crude oil "A". This demonstrates that low salinity fluids play an important role in the wettability change processes.

The oil recovery in a secondary process using seawater reached a plateau of 36.87 % of OOIP after 4 PVI. The injection fluid was then changed to LSSW10, which resulted in a small increase in oil production with a maximum plateau of 40.62 % after 8 PVI. Previous experiments with the same core and a basic crude oil resulted in higher oil production for low salinity water but slightly lower production for seawater.

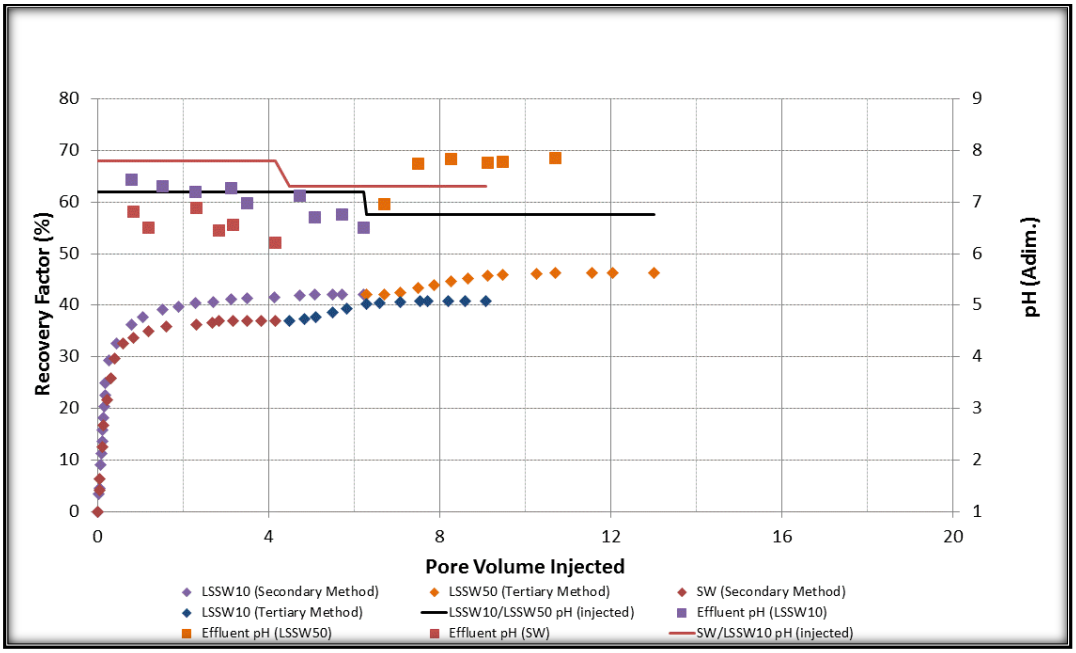

Figure 5.28: Oil recovery versus pore volumes of injected water at 92^{o} C.

Figure 5.29 illustrates the variations of ion concentrations in terms of pore volumes injected for the low salinity waters system. The concentration of magnesium and sulphate ions did not change for the first period of injection with LSSW10. This is comparable to what was previously observed for the basic crude oil, as shown in Figure 5.24. The effluents maintained a continuous production of calcium and bicarbonates. When the concentration of the injected fluid was dropped, the production of these ions

remained high. As the change in concentration became great enough, the effluents continued producing bicarbonates but the sulphate exhibited a sudden change. This change is perceptible from 7 to 10.70 PVI. The effect of this additional production during the whole experiment can be explained by considering the probable removal of the core damage. Notice also that this low salinity water (LSSW50) has the ability to be less saturated, as explained in subsection 4.3.1.1., revealing that the salts in the brine may increase. These results were later confirmed with the permeability measurement, where the final value was 158.57 md, as shown in Table 5.7. As the low salinity water was injected, the damage was practically removed. The lower the concentration of the brine, the more active the brine will become. Due to contamination with the previous water samples, no analyses were obtained from 10.7 to 13 pore volumes injected.

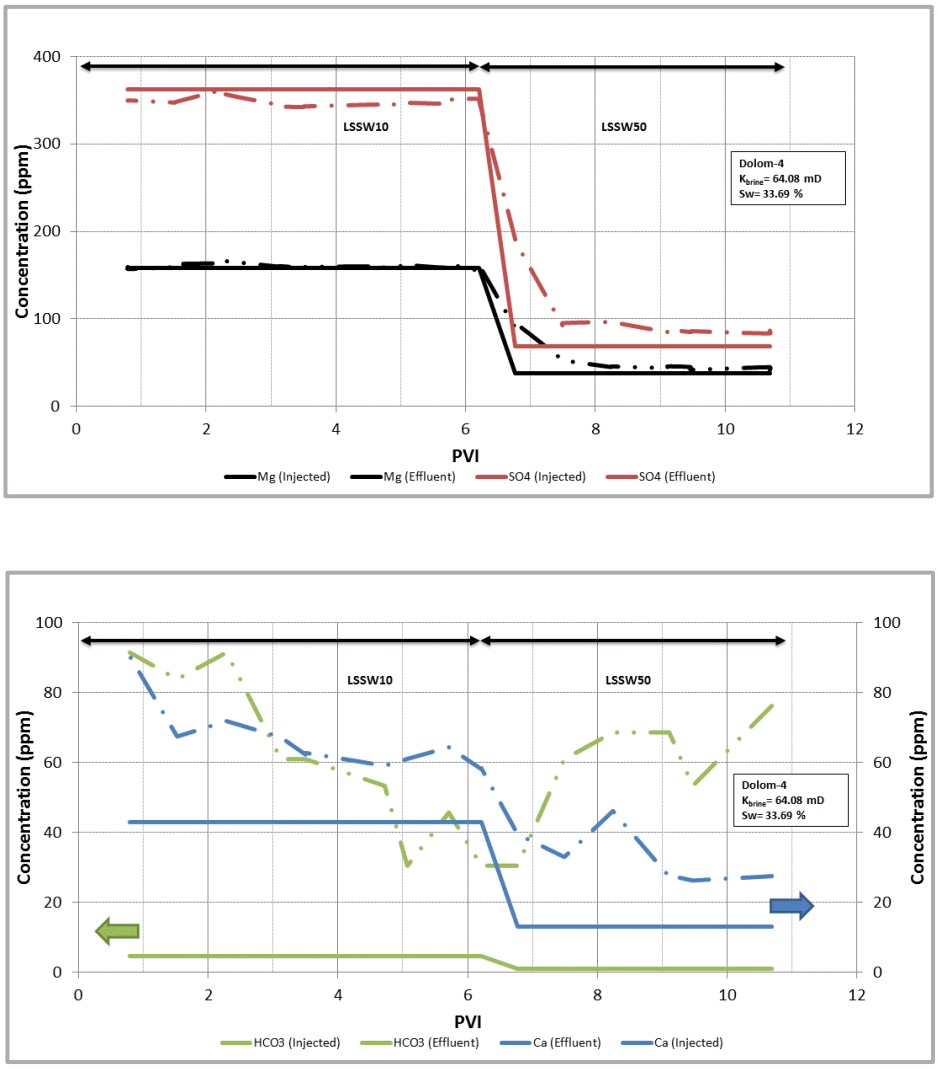

Figure 5.29: Changes in ion concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- when low salinity waters were injected through the dolom-4 core at 92^o C using an acidic crude oil (Crude oil "E").

Table 5.7: Changes in core permeability after the coreflood experiments for two crude oils.

Core Number	Initial k_{brine} (md)	Process	Injected Fluid	RF (%)	Final k_{brine} (md)
Crude Oil "A"					
Dolom-4	142.21	Secondary	LSSW10	69.30	180.28
Dolom-4	180.28	Secondary	Seawater	32.43	64.08
Crude Oil "E"					
Dolom-4	64.08	Secondary/Tertiary	LSSW10/LSSW50	42.05/4.29	158.57
Dolom-4	158.57	Secondary/Tertiary	Seawater/LSS10	36.87/3.75	141.83

The oil recovery factors, changes in core permeability and ion concentration variations imply that the mechanism of rock dissolution is practically negligible for the experiments using an acidic crude oil (crude oil "E"). Moreover, the wettability change, where it occurred, was relatively lower.

In Figure 5.30, only very small pressure variations can be noticed during the injection processes. Injection at a high rate caused a rise in pressure to a maximum value of 3 psi. Modification of the rate was not accompanied by an increase in oil recovery. The pressure continued to drop smoothly and stabilised after a while. Additional oil recovery was never gained with high injection rates. In spite of the fact that the permeability changed, no direct experimental evidence is accessible to support the possibility that either dissolution or blockage can be detected by analysing differential pressure across a core, so far. No significant changes can be observed in the pressure behaviour, apart from injection rate adjustments at the end of each sequence.

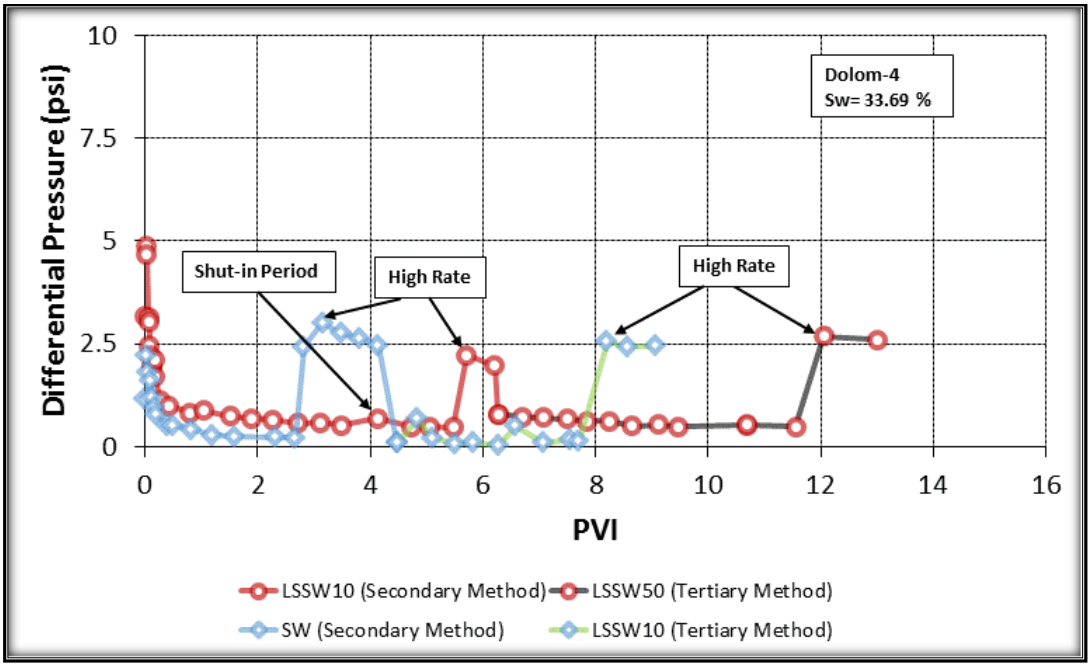

Figure 5.30: Differential pressure across core versus pore volumes for the Dolom-4 core with four brines.

CHAPTER 6 – CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

In this work, practical analysis helped to elucidate the real importance of the crude oil/injection water interactions. The tests that were presented in *Chapter 4* essentially provide an insight into the impact of the chemical interaction between crude oil and injection water with the rock. Based on direct evidence, basic assessments aided in understanding why: a) the solubility of certain oil compounds (water-soluble compounds) increases in the aqueous phase, b) the crude oil is detached from the rock surface when the equilibrium in the system is broken, c) rock dissolution takes place, d) the effluents from the injection water have variations in their ionic concentrations, and finally e) the pH of these effluents is increasing in value. In the past, the influence of crude oil properties has largely been overlooked because it was assumed that both crude oil and injection brine were immiscible or remained unaffected in contact with each other. The findings from recent works have challenged this assumption and the research in this thesis corroborates these findings and confirms that crude oil/injection water interactions do really occur.

This research has allowed that even in basic analysis, the interaction between the crude oil and the injected water is meaningful. In reality, *the chemical interaction between crude oil and injected water is one of the main reasons for the increased efficiency in response to the use of the smart waters for the improvement of oil production.*

The major advantage of using basic analytic techniques is their ability to validate or predict the presence or absence of a variety of phenomena. The permeability measurement tests also elucidated the importance of fluid interactions. The variation in the permeability values using injection water in contact with crude oils was a direct response to the dissolution of the rock caused by the previous interactions between crude oil and injection water. At the same time, it was found that not all crude oils could generate the *acidic water* which is the *cause of dissolution of the rock*.

Existence of rock dissolution, as a mechanism for oil production, is known and has previously been documented (Yousef et al., 2010-2012; Zahid et al., 2012; Nasralla et al., 2014); however, the reasons for its presence have not entirely been found or described. *This research shows that dissolution occurs as a direct and strong effect of the flow of injected water in contact with the crude oils*. The original injected water turns out to be more acidic when in contact with crude oil, generating *new and different injected water*. This new form does not change its ionic concentration, but only changes its acidity. Its presence under static conditions, as stated in the body of this work, is practically undetectable, because the dissolution is likely to be slower and both time- and rate-dependent.

The *water-soluble compounds dictate whether acidic water is generated or not*. For the basic crude oils tested in *Chapter 4*, all of them generated acidic water, from low salinity water to distilled water. On the other hand, acidic crude oil was the only one that did not generate acidic water, but this does not mean that there is a rule for all the crude oils. The key parameter is the amount of water-soluble compounds that the crude oils contain.

As evident from the results of *Chapter 5*, neither contact angle measurements nor spontaneous imbibition tests were able to identify the presence of the dissolution mechanism. This is because:

- The contact-angle measurements only allowed us to evaluate the potential of the smart waters in terms of wettability modifications. Smart waters (especially low salinity water) altered the natural state of wettability to be less oil-wet for a basic crude oil. However, smart waters did not promote significant changes in wettability, except for low salinity water.

- Spontaneous imbibition tests showed a favourable response to smart waters. The final oil recoveries observed for spontaneous imbibition tests using smart fluids were around 30 %, which confirmed the improvement of oil recovery. With regard to rock dissolution, these tests were not able to observe an acidic system which could have

improved the oil production. This meant that the main mechanism that triggers the additional oil production, is the change of wettability.

The results of the coreflood experiments performed in this work with smart waters, demonstrate that a substantial additional amount of heavy crude oil can be obtained under secondary as well as tertiary injection.

Mechanisms that trigger oil production for the studied crude oils are linked to both changes of wettability and effect of the rock dissolution. Effluent analysis and permeability evaluations validated the effect caused by low salinity water as acidic water in contact with the rock.

As was seen in *Chapter 5*, the presence of rock dissolution is principally detected by coreflood experiments and its occurrence is small under static conditions. There is no doubt that the effect would be more important at reservoir scale. These findings differ from those of Mahani et al. (2015), where they affirmed that the rock dissolution was only relevant on a laboratory scale and not at reservoir scale. Inevitably, we all sometimes see things subjectively, to some extent, or with the lack of strong evidence.

Damage to the cores occurs if seawater is used for enhanced oil recovery methods. Permeability measurements corroborated these findings. In addition, neither high temperatures nor divalent ions contained in the injection water helped to improve the oil production. Specific conditions that were pointed out by RezaeiDoust et al. (2009) for the wettability alteration effect when seawater is used in an enhanced oil recovery process were not observed during this research.

Special care should be taken when the ion concentrations' variations are evaluated, because the analysed volumes are very small. This may thus introduce errors or poor reproducibility. It is important to have good accuracy in the results and every sample should be duplicated.

It was also possible to explain the absence of a dissolution mechanism for an acidic crude oil. The improvement in oil production was based on the wettability alteration for this crude oil. Permeability measurements helped to determine that the mechanism of rock dissolution was practically negligible for this acidic crude oil.

In spite of the fact that the permeability changes occurred, no direct experimental evidence is accessible to support the possibility that either dissolution or blockage can be detected by analysing differential pressure across a core, so far.

The *suggested model* in Figure 4.8, as previously stated, supports the assumption that basic crude oils can be susceptible to *donating hydrogen ions* in the case analysed, *generating acidic water*. This *proposed model* cannot be generalised to all basic crude oils or ruled out for all acidic crude oils. The components of crude oil, as observed, will dictate what type of interactions will occur between the injected water and the crude oil.

The inclusion of the bicarbonate concentration analysis from the effluents is relevant because this would aid in clarifying the presence of dissolution of the rock.

6.2 FUTURE WORK

The main results obtained in this PhD work have indicated that the nature of the acidic species in the crude oil enables them to become important agents and firstly cause a reaction between the crude oil and the brine of low salinity. The solubility of certain oil compounds increases in the aqueous phase, due to the low salinity concentration. This effect on oil recovery from the low salinity water is partly due to the chemical reaction between the diluted water and the acids that exist in the crude oil.

Despite its high content of acidic compounds, the initial results with acidic crude oils revealed that the acidic water cannot be created using these crude oils. These results question the link between a high amount of acidic components and generation of acidic water and unequivocally indicate that it is not conclusive or sufficient. Therefore, it is

suggested to investigate in more detail the content of water-soluble compounds in the acidic crude oils.

Researchers have focused on oil-soluble compounds because they act with the rocks regarding wettability; however, the water-soluble compounds have been ignored or ruled out. More effort is needed to better understand the influence of such water-soluble compounds in oil production. Therefore, more research needs to be conducted to better understand which group of water-soluble compounds migrates to the water easily or which specific water-soluble compound is actively interacting with the injected waters.

A similar model to that described in *Chapter 4* could be designed for acidic crude oils in carbonate formations. This model would help us to understand the presence or absence of certain mechanisms previously mentioned in the published literature.

Although spontaneous imbibition tests at high temperature are considered a convenient way to evaluate the potential of oil production, especially with naturally fractured reservoirs, it is recommended to include some tests at high pressure. These tests would facilitate the understanding of the impact of the pressure on the rock dissolution under static conditions. This type of test should also be used to highlight the difference in the enhanced oil recovery between basic crude oil and acidic crude oils.

Additional coreflood experiments should be performed with more basic crude oils in order to validate the assumption of the rock dissolution mechanism in carbonate rocks.

Considering that the damage in the cores was identified during the injection of seawater, a similar procedure, as described in section 4.3.1.2, should be applied for evaluating changes in the composition of the fluids and pH values. This is critical because results in this PhD work showed a decrease of the pH values throughout the experiments with seawater (see subsection 5.4).

In this work, all experimental tests were performed with cores placed horizontally. To investigate the effects of gravity forces, it is required to run a few experiments with cores placed vertically. Additionally, the injection mode, either from the top to the bottom or vice versa, should also be evaluated for experiments of this type.

Carbonate oil reservoirs are normally associated with high salinity formation water (up to 300, 000 ppm), which increases the difficulty of injecting the water for enhanced oil recovery methods and hence reduces the options for producing more crude oil. It is thus recommended to run coreflood experiments where both high salinity formation water and low salinity water injection are considered.

A recent technical paper by Sanchez-Rodriguez et al. (2015) underlined the importance of sensitivity studies, such as the effect of changes in injection rate or injection time, well spacing, reservoir thickness, heterogeneities or changes of permeability; all these effects were also considered for heavy crude oil in carbonate formations. This study for heavy crude oils addressed the real impact of smart water injection in oil reservoirs. The results were attractive and promising. Thus, more simulation studies would be needed to investigate whether the expected benefits of these effects are exhibited at reservoir scale using low salinity fluids.

Generation of acidic water was also observed in other types of waters in contact with crude oils. These preliminary results indicate that the transfer of water-soluble compounds from the crude oil to the analysed water is not exclusive to diluted waters. The movement of such compounds could be inferred to other types of water, even those with high salt concentrations. Even though these findings were not included in the work of this research, it is highly recommendable to study the interactions between all crude oils and candidates for water injection in carbonate oil reservoirs.

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